647
29/12/97
LUDHIANA
Lib
29/12/97

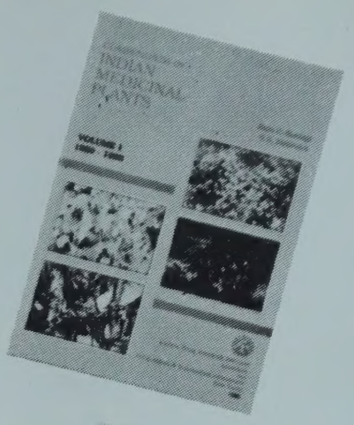
J SCI IND RES
NOVEMBER 1997
CODEN: JSIRAC 56(11) 651 - 716 (1997)
ISSN: 0022-4456

JOURNAL OF SCIENTIFIC & INDUSTRIAL RESEARCH

(Incorporating *Research and Industry*)

Published by
NATIONAL INSTITUTE OF SCIENCE COMMUNICATION, CSIR
NEW DELHI

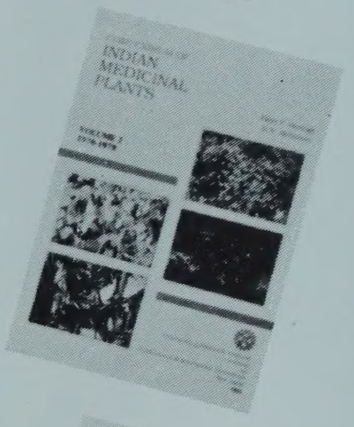
Compendium of Indian Medicinal Plants



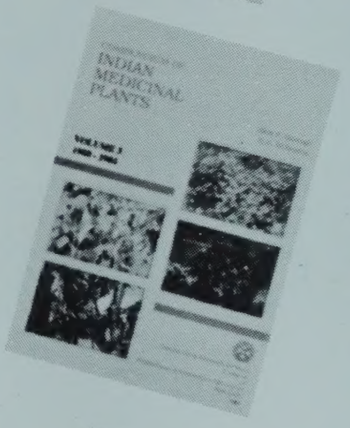
4 Vols.

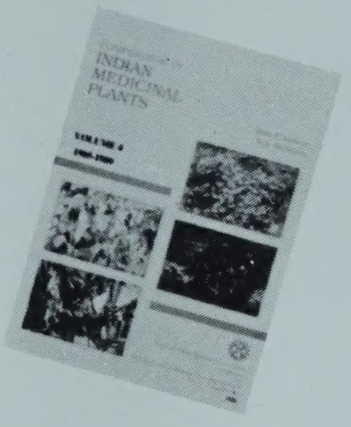
by R P Rastogi and B N Mehrotra

Vol.1 Reprinted with Addendum 1993. Pp515. Price Rs 300; Postage Rs 15.
Vol.2 Reprinted with Addendum 1993. Pp 859. Price Rs 550; Postage Rs 15.
Vol.3 1993. Pp 831. Price Rs 600; Postage Rs 15.
Vol.4 1995. Pp 930. Price Rs 750; Postage Rs 15.



The volumes provide information on all the compounds obtained from Indian plants that have medicinal properties. Chemical structures of these compounds break the monotony of the text. The isolation of these compounds from the plants and the description of their biological activities boost the usefulness of the compendium. The names of plants, families and orders of plants have been updated. Additional information in the volumes appears in the form of three indexes comprising local names, chemical constituents and biological activities. The first volume describes almost 1200 plants covering the ten year period 1960-69. The second volume covers the period 1970-79 and describes 1684 plants. The third volume covers the period 1980-84 and describes 1600 plants. The fourth volume covers the period 1985-89 and describes 1650 plants. The volumes include research done all over the world on medicinal plants found in India, whether indigenous or introduced. The volumes are useful for botanists, chemists and all those working on medicinal plants/natural products.





Order should be accompanied by Money Order/Demand Draft/IPO made payable to National Institute of Science Communication, New Delhi and sent to:

Sales and Distribution Officer
National Institute of Science Communication
Dr. K.S. Krishnan Marg, New Delhi-110012
Ph: 5785359, 5786301/7
Fax: 011-5787062, Telex: 031-77271

Journal of Scientific & Industrial Research

(Incorporating *Research and Industry*)

Editorial Board

Dr V.P. Bhatkar
Executive Director
Centre for Development of
Advanced Computing
Pune University Campus
Ganesh Khind
Pune-411 007

Dr M M Doshi
Executive Director (Technical & Production)
J.B. Chemicals & Pharmaceuticals Ltd.,
Neelam Centre, 'B' Wing, 4th Floor,
Hind Cycle Road, Worli,
Bombay-400 025

Dr T.R Govindachari
Director,
SPIC Science Foundation
Centre for Agrochemicals Research
Mountview
110, Anna Salai, Guindy
Madras-600 032

Shri M N Gupta
Chief Engineer (Metallurgy)
National Research Development Corporation
Anusandhan Vikas
20-22 Zamroodpur Community Centre
Kailash Colony Extention
New Delhi-110 046

Prof. L C Jain
Above Diksha Jewellers
554 Sarafa
Jabalpur-482 002 (M.P.)

Shri Ashok M Kadakia
Chairman & Managing Director
Ashok Organic Industries Ltd
406 Sharda Chambers
33 Sir Vithal Thackersey Marg
(New Marine Lines), Bombay 400 020

Dr Noboru Miyawaki
Executive Vice-President
R&D Headquarters
N.T.T. Corporation
1-6 Uchisaiwai-cho-i-chome
Chiyoda ku
Tokyo-110-19, Japan

Dr Nitya Nand
Former Director
Central Drug Research Institute,
Chattar Manzil
Lucknow-226 001

Dr S Pal
Group Director
Communications Systems Group
ISRO Satellite Centre
Department of Space, Govt of India,
Airport Rd, Vimanapura P.O.
Bangalore-560 017

Dr M Patel
Director
Pulp & Paper Research Institute
Jaykaypur-765 017
Orissa

Dr S Ramanathan
c/o TIFAC
Department of Science &
Technology
Govt of India, Technology Bhawan
New Delhi-110 016

Shri Y S Rajan
Senior Adviser — Technology
Confederation of Indian Industry (*CII*)
India Habitat Centre
4th Floor, Zone IV, Lodi Road
New Delhi 110 003

Dr V Rajaraman
Chairman
National Centre for Science Information
Indian Institute of Science
Bangalore-560 012

Dr T S R Prasada Rao
Director
Indian Institute of Petroleum
P O IIP, Mokhampur
Dehradun, 248 005

Prof. M M Sharma
Professor of Chemical Engineering and
Director,
Department of Chemical Technology,
Matunga, Bombay-400 019

Prof. S P Sukhatme,
Professor of Mechanical Engineering
Indian Institute of Technology,
Powai, Bombay-400 076

Dr Sushil Kumar
Director,
Central Institute of Medicinal and
Aromatic Plants, P.O. CIMAP
Lucknow-226 015

Dr Joseph Thomas
Vice-President (Biotechnology)
Southern Petrochemical Industries
Corporation Ltd
97, Mount Road
Madras 600 032

Prof. Atul Kohli
Professor of Politics &
International Affairs
Woodrow Wilson School of
Public and International Affairs
Princeton University
Bendhein Hall,
Princeton, New Jersey-08544-1022
USA

Prof. (Mrs) P Vasudevan
Head, Centre for Rural
Development & Technology
I.I.T., Hauz Khas,
New Delhi-110 016

Editor-in-Chief, *Ex-officio*

Editors: **Dr S A I Rizvi, D S R Murty, H K Khanna, Dr B S Aggarwal, H S D Khatri**

Director:
National Institute of Science Communication,
Dr K S Krishnan Marg, New Delhi 110 012

Phone: 5746024 Telex: 031-77271 PID IN Fax: (0091)-11-5787062
Telegram: PUBLIFORM, NEW DELHI E-mail: 'niscom'@ sirnetd.ernet.in

The Journal of Scientific & Industrial Research is issued monthly. The Institute assumes no responsibility for the statements and opinions advanced by contributors. The editorial staff in their work of examining papers received for publication is assisted, in an honorary capacity, by a large number of distinguished scientists working in various parts of India and abroad.

Communications regarding contributions for publication in the journal and books for review should be addressed to the Editor, Journal of Scientific & Industrial Research, National Institute of Science Communication, Dr K S Krishnan Marg, New Delhi 110 012.

Correspondence regarding subscriptions and advertisements should be addressed to the Sales & Distribution Officer, National Institute of Science Communication, Dr K S Krishnan Marg, New Delhi 110 012.
Phone 5786301-07 Gram:PUBLIFORM Telex:031-77271 PID IN

Annual Subscription

Rs 500.00	$ 200.00*	£ 125.00*

Single Copy

Rs 50.00*	$ 20.00*	£ 15.00*

Payments in respect of subscriptions and advertisements may be sent by cheque, bank draft, money order or postal order marked payable to National Institute of Science Communication, Dr K S Krishnan Marg, New Delhi 110 012. Cheque/Demand draft may be drawn in favour of 'NATIONAL INSTITUTE OF SCIENCE COMMUNICATION, NEW DELHI'. Bank charges shall be borne by the subscriber; for inland/outstation cheques please add Rs 10.00 and for foreign cheques please add $ 2.00 or £ 1.00.

Supply of the journal will commence on receipt of subscription in advance.

*The rates of annual subscription and single copy include first class mail charges.

Claims for missing numbers of the journal will be allowed only if received within three months of the date of issue of the journal plus the time normally required for postal delivery of the journal and the claim.

© 1997 The Council of Scientific & Industrial Research, New Delhi.

Journal of Scientific & Industrial Research

(Incorporating *Research and Industry*)

VOLUME 56 **NUMBER 11** **NOVEMBER 1997**

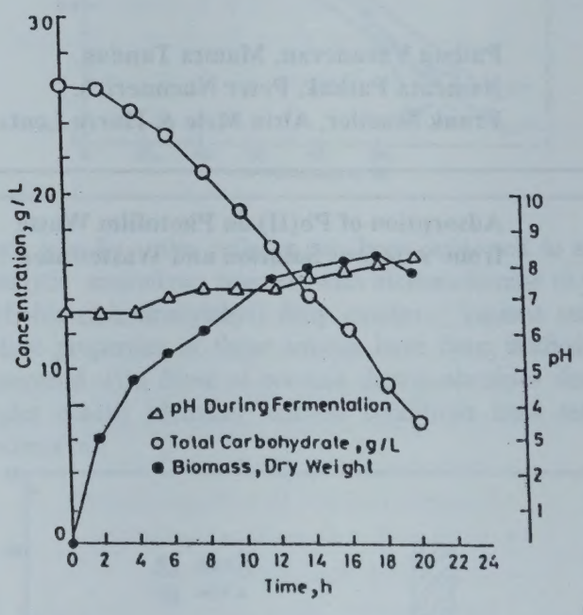
CONTENTS

Review Papers

651 **Biocides, *Bacillus sphaericus* and *Bacillus thuringiensis* as Potential Mosquito Larvicidal**

S R Naik

The newer biological control agents, biopesticides, viz. *Bacillus sphaericus* and *Bacillus thuringiensis* have shown excellent mosquito larvicidal activity, which could be used effectively in integrated disease vector control programme. The results of extensive large-scale field trials have indicated that both the pesticides are environment-friendly and also exhibit broad range of pesticidal activity with target specificity. The acceptance of these biopesticides as mosquito control largely depends upon various factors like, cost-effectiveness, *per se* effect on various environmental safety, changing stage, and federal regulation.



657 *Salvadora persica* — A Boon to Wasteland Development

It is suggested that in the pursuit of using neglected resources, a new scientific concept of using wastelands has to be envisaged. The saline/alkaline lands are spread over 9m ha in India and are distributed both in inland and coastal regions. *Salvadora persica* is one of the most promising plants to be grown on such lands. This plant has immense industrial applications. The wood of this plant is useful in the timber industry. The paper elucidates the utilization of wastelands by growing *Salvadora persica* which has various applications.

S T Zodape & V K Indusekhar

Papers

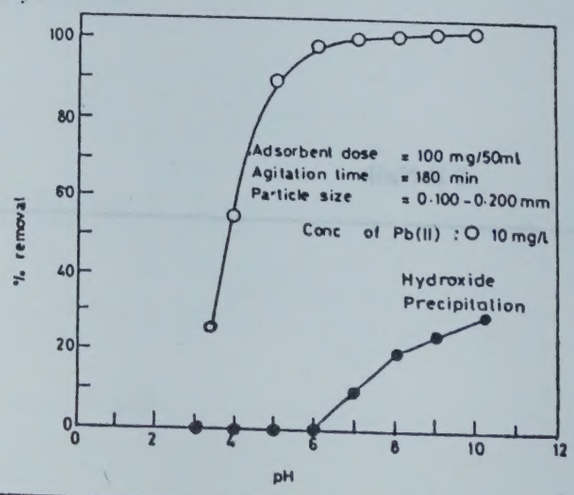
662 **Fluid CO_2 Extraction and Hydrodistillation of Certain Biocidal Essential Oils and Their Constituents**

Natural products, traditionally used as insecticides, bacteriocides, fungicides and pharmaceuticals, have once again gained importance because of the harmful effects of synthetic products. The qualitative and quantitative composition of the extracts from natural products, however, vary depending upon the extraction conditions. Extraction studies on four common herbs, *Murray koenigü*, *Lantana camara*, *Ocimum sanctum* and *Tagetes patuala* are described using liquid CO_2, supercritical fluid CO_2 and hydrodistillation. A comparison of the extracts obtained is presented.

Padma Vasudevan, Mamta Tandon, Namrata Pathak, Peter Nuennerich, Frank Mueller, Altin Mele & Harro Lentz

673 **Adsorption of Pb(II) on Photofilm Waste from Aqueous Solution and Wastewater**

Photofilm industrial waste sludge has been studied as a sorbent for removal of Pb(II) from aqueous solutions. Effects of contact time, initial concentration of Pb(II), adsorption dosage, particle size and pH have been studied. The efficiency of the adsorbent to remove Pb(II) was found to be 99 per cent for the wastewater obtained from radiator industry.

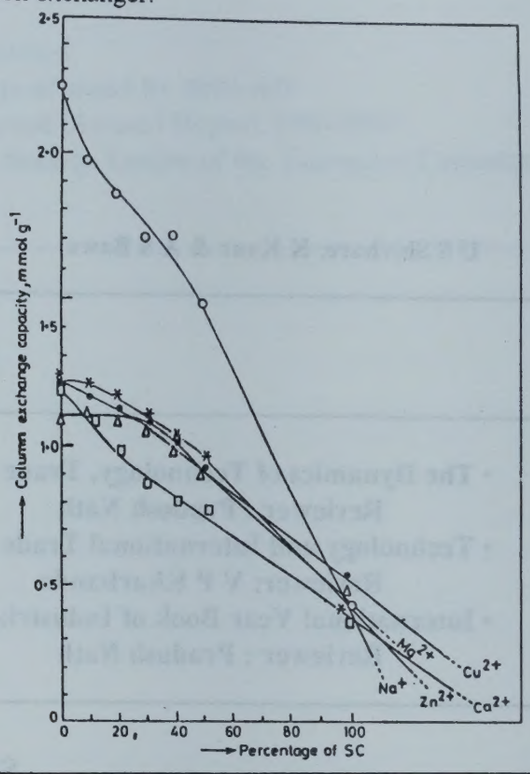


K Selvaraj & V Chandra Mohan

680 **Synthesis and Characterization of New Composite Ion Exchangers**

A Mariamichel & S Krishnamoorthy

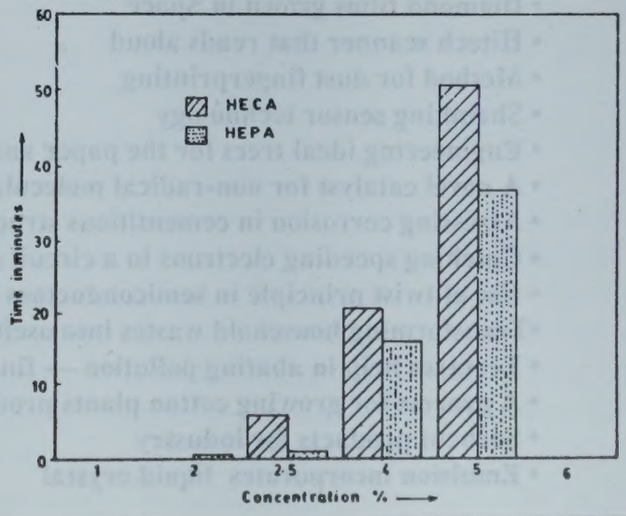
The charcoal obtained by sulphonating the tannin rich mangroves bark has been used to replace the polymeric matrix of phenolformaldehyde sulphonic acid. A few cation exchangers are obtained by varying the substituent content from zero to 100 per cent. The important characteristics of the composites have been determined. Since the composites up to 30 per cent substitution retain the essential properties of pure phenolic cationite and also that the mangroves bark is available freely and in plenty, it is established that the 30 per cent composite is a cheaper cation exchanger.



686 **Surface Active Properties of N,N-bis (2-Hydroxyethyl) Fatty Amides Derived from Pilu Fat**

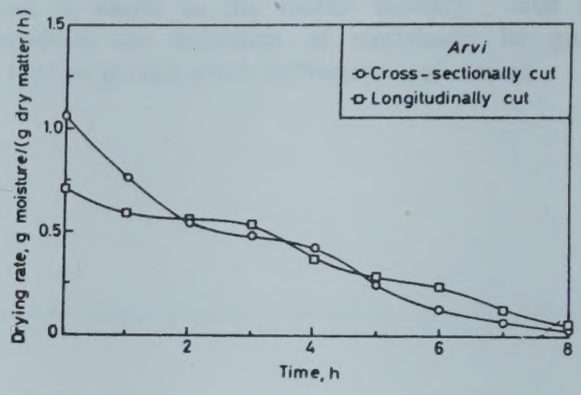
R P Patel & V M Mannari

Raw pilu fat after refining has been subjected to alkali catalytic aminolysis reaction with diethanolamine to yield N,N-bis (2-hydroxyethyl) fatty amides. Various surface active properties of these amides have been studied and compared with those of coconut diethanolamides derived under exactly identical reaction conditions from refined coconut oil.



691 **Studies on Drying of Arvi**

Drying of arvi (*Colocasia*) has been carried out in a cabinet dryer at 57°C. The drying rate curves indicate that the drying of arvi takes place in the falling rate period. The Page's model adequately describes the drying behaviour of arvi.



U S Shivhare, K Kaur & A S Bawa

Book Reviews

696 • **The Dynamics of Technology, Trade and Growth**
Reviewer : Pradosh Nath
• **Technology and International Trade**
Reviewer: V P Kharbanda
• **International Year Book of Industrial Statistics**
Reviewer : Pradosh Nath

Sci-Tech Update

700 • **UNEP-OzonAction Programme — A new software released**
• **Microprocessor controlled filter reduces vehicular pollution**
• **Microelectronic device implant to stimulate nerves**
• **New microscopic semiconductor crystals for basic research**
• **Diamond films grown in Space**
• **Hitech scanner that reads aloud**
• **Method for dust fingerprinting**
• **Shrinking sensor technology**
• **Engineering ideal trees for the paper and pulp industry**
• **A novel catalyst for non-radical molecular oxygen activation reported**
• **Assessing corrosion in cementitious structures by using NMR**
• **Catching speeding electrons in a circuit city**
• **Use of twist principle in semiconductors**
• **Transforming household wastes into useful materials!**
• **Ecotaxes help in abating pollution — finds OECD report**
• **A process for growing cotton plants producing cotton/polyester hybrid fibres developed**
• **Sorbent products for industry**
• **Emulsion incorporates liquid crystal**

Sci-Tech Update

- **Machine that 'prints' tablets to order developed**
- **Renewable source of human neurons created**
- **New technique maps the body electric**
- **New study links slimming drugs to heart disease**
- **High dose of vitamin can cause permanent nerve damage**
- **First Bi-Bi double bond obtained**
- **A clean method for aromatic brominations reported**
- **Report on the growth of petrochemical products demand by 2001 AD**
- **National Dairy Research Institute (NDRI), Karnal: Annual Report 1996-1997**
- **Report of the Working Groups of Information Society Forum of the European Commission**
- **Announcement**

Journal of Scientific & Industrial Research
Vol. 56, November 1997, pp 651 - 656

Biocides, *Bacillus sphaericus* and *Bacillus thuringiensis* as Potential Mosquito Larvicidal

S R Naik

Research & Development Division, Hindustan Antibiotics Limited, Pimpri, Pune 411 018, India

Received: 06 February 1997; accepted : 08 July 1997

The newer biological control agents, biopesticides, viz. *Bacillus sphaericus* and *Bacillus thuringiensis* have shown excellent mosquito larvicidal activity, which could be used effectively in integrated disease vector control programme. The results of extensive large-scale field trials have indicated that both the pesticides are environment-friendly and also exhibit broad range of pesticidal activity with target specificity. The presence of Multiple ICPS in these biopesticides may delay resistance or make it resistance-free. *Bacillus thuringiensis* is extremely toxic to *Aedes aegyptii* and Culex and less toxic to anopheline larvae, whereas, *B.sphaericus* is more toxic to culex, *A.stephensi*, *A culicifacies* and less toxic to *Aedes aegyptii*. All these mosquito species are implicated as an important vector of malaria, filariasis, encephalitis, and dengue. *B.sphaericus* and *B.thuringiensis* is produced by submerged fermentation and cells are separated after harvesting the fermented broth. The potency of the biopesticide is determined using I and II instar larvae of mosquito species, Anopheles, Culex and Aedes. Various formulations in the form of granular, wettable or dust powder are prepared for final application in the field. The acceptance of these biopesticides as mosquito control largely depends upon various factors, viz. cost-effectiveness, *per se* effect on environmental safety, changing stage, and federal regulation.

Introduction

Most of the insect diseases are caused by bacteria,fungi, protozoa, microspora, and viruses. These organisms are collectively referred as entomopathogens. Several references are available suggesting that natural enemies being employed to control pests[1,2], e.g. in the year 1200 AD Chinese citrus growers purchased nests of the predacious anti-oceophylia smaragdina and placed them in citrus tree to control a caterpillar, *Tessarotoma papiltosa.*

Although many bacteria are pathogenic towards insects, a few have been exploited as biological control agents. Insect pathogenic bacilli include strains of *B.thuringiensis*, *B.lentimorbus*, *B.sphaericus* which are among the widely known and researched bacteria[3]. These bacteria have been further developed by genetic manipulation (e.g. expression of toxin genes) to increase its infectivity towards specific insect(s) and thereby harnessing its benefits in pest-control management.

Most of the work on biotechnological approaches to vector control measures is concentrated on pathogens[4]. Their efficiency can be enhanced through molecular approaches by cloning with genes of desired origin and nature to increase the virulence of existing pathogens, for constructing 'superpathogens' which are far more effective in attacking the pests. Other approaches are designed to increase or change the range of organisms affected by the pathogens. However, its nonspecificity causes all the problems of chemical sprays in terms of its effect(s) on the whole environment.

Many fungal isolates have also shown larvicidal activity but their identity and mode of action are yet to be investigated and understood[5]. A significant mosquito larvicidal activity was shown specifically against *Culex quinuiifasciatus* and *A. strephensia* by the secondary metabolite obtained from *Streptomyces griesus*. Hence, development of many new generation biopesticides can be achieved by good and effective screening programme.

Microbial Pest Control Agents : Necessity and Development

For the past several decades, broad spectrum chemical pesticides have been used indiscriminately and have saved millions of lives that might otherwise have been lost to insect-borne (vector- borne) diseases. Furthermore, these chemicals have also contributed to the substantial increase in farm yields that have occurred during this period.

However, these improvements and achievements in the quality of life have come at a high cost that has only become evident within the past two decades[6].

The high toxic residues of the synthetic insecticides have already become environmental contaminants (xenobiotics) causing toxic effects on wild life, including birds, beneficial insects like honey bees and conceivably produced adverse effects on human being as well. In addition, indiscriminate usage of insecticides has fostered the emergence of resistance pest variants that are no longer killed by the chemicals and also induced harmful effects on non-target insect pests such as predators, parasites, etc.[6] Microbial pesticides, particularly *B.thuringiensis var israelensis* and *B.sphaericus* have undergone considerable development and their several large-scale field trials have been carried out to control mosquito vectors. However, these trial reports have indicated that vector control could be achieved to a great extent but disease control has yet to be demonstrated and established except in the case of onchocerciasis in West Africa.

Advantages of Biopesticides

- High specificity and efficacy towards the target organisms.
- Enhancement of effect is assured even at the cellular level, as one-third of the cell mass is the insecticidal biopyradmidal crystal protein.
- Today, a wide variety of *B.thuringiensis* and *B.sphaericus* strains with broad range of pesticidal activity that include flies, worms, mites and nematodes with target specificity are available, thus enlarging the target spectrum.
- Better understanding of molecular genetics.
- Flexibility in growth requirements, low developmental cost and environmental compatibility when compared to other conventional agro-chemicals.
- Effective production strategies have ensured economy of these bio-products.
- The presence of multiple ICPs may delay resistance.
- Biopesticides are completely compatible with natural control agents such as fish and nematodes, low or no toxicity to man, domestic animals or non-target biota in the environment.
- Biopesticides can make an important contribution to an integrated disease vector control programme.

Dr S R Naik obtained MSc (Biochemistry) and PhD (Pharmacology) from Bombay University in 1968 and 1973, respectively. He was awarded International Fogarty Fellowship for 2 y to carry out post-doctoral research at National Institute of Health, USA in the area of Psychoneuropharmacology. After returning Dr Naik was offered Scientist 'C' in CSIR and actively involved himself in simulation of animal models to understand patho-physiological changes of different diseases and also to employ such models for screening pharmacologically active compounds. He joined R&D division of Hindustan Antibiotics Limited, Pimpri in 1978 as Deputy Manager and from 1987 onwards he is working as General Manager, Research & Development. He was Visiting Professor of Pharmacology during 1980-82 at School of Pharmacy & Pharmaceutical Technology attached to Federal University, Paraiba, Brazil. As a Visiting Professor, he has established modern laboratory for carrying out research work in the area of chemistry and pharmacology of Natural Products and initiated post-graduate course in Natural products. He has 27 y research experience in the area of Drug Research and Drug Development. He has so far published 110 research papers (peer-reviewed) in reputed national and international journals and has many patents to his credit. He has been awarded NRDC National award in 1995 and Hexamar Agricultural Research Foundation Award in 1996. He is a Fellow of Royal Society of Chemistry, London. Many students completed post- graduation and received advanced training under his guidance. He is an active member of many scientific and technical bodies and academic institutions. He is very proficient in industrial R&D management.

The major differences in *B.thuringiensis* and *B.sphaericus* are as follows :

B.thuringiensis	B.sphaericus
(i) First isolated in Israel by Goldberg and Margalit.[7]	(i) First isolated by Kellen *et al.*[8] and later highly toxic strain by Payne and Davidson.[9]
(ii) Effective against two major genera of Mosquitoes, *Aedes aegyptii* and *Culex* and l followed by *culicifacies* and *anopheline* larvae. Less effective to malarial genus *Anopheles* may be due to its surface feeding behaviour.	(ii) *B.sphaericus* is most toxic to *Culex* arvae followed by *A stephensi* and *A.culicifacies* but less toxic to *Aedes aegyptii*.
(iii) A short residual field efficiency larvae hatching 1 to 2 d after its application are not affected.	(iii) Generally shows a longer residual effect, reportedly several months possibly due to recycling.
(iv) Efficient in clear water.	(iv) Performs well even in polluted habitats.

Development of *B.sphaericus* and a Potential Mosquito Larvicidal

Malaria, filariasis,encephalitis and dengue continue to be major public health problems transmitted by mosquitoes in tropical zone. Onchocerciasis and Leishmaniasis are transmitted by black flies and sand flies and pose a major health problem in Africa and certain parts of India.The prevention and control of these diseases which are closely linked to ecological factors, still depends largely on antivector measures using insecticides. Control of mosquitoes and the diseases transmitted by them has become problematic owing to a multiplicity of factors.

Taking into consideration these reasons, academic, governmental, and industrial scientists have been actively exploring how pest might be controlled with natural or biological agents. It was thus found that this can be achieved in any of the following ways: (i) The release of sterile male insects to mate non-productively with females of the pest species, (ii) Application of pheromones to impair insect feeding or reproductive behaviour, (iii) The most ideal would be biological pest control using microorganisms that have innate ability to produce toxins specifically to kill certain insects or group of insects. Therefore, microbial control of insects is an attractive proposition as microbes generally have very narrow host ranges. It is assumed that more than 1500 biological agents or biocides could be developed having commercial potential.

Today, worldwide, insecticides sales are between $ 6 to 8 billion and total sale of *B.thuringiensis* based biopesticides is estimated to be more than of $ 100 million. It is reported that the volume of sale ($ 57 million) in the US itself is almost equal to combined sale volume of other developing and the developed countries (Data from Rigby, 1991) which emphatically suggests a great commercial potential for this product. Technologies for *B.sphaericus/B.thuringiensis* have already been developed by Anna University, Chennai and Central Drug Research Institute (CDRI), Lucknow and also large-scale field trials were carried out in some parts of Northern and Southern India[10,11]. The results of these trials are quite encouraging. Researchers at the Hindustan Antibiotics Limited (HAL), Pune have extended their expertise and facilities to both these institutes to scale-up the biopesticide process technology and also produced these biopesticides in large quantities at HAL plant for carrying out their field trials and other important biological and toxicological evaluation.

Here an attention is focused on biological control of mosquitoes using (*B.thuringiensis* and *B.sphaericus*) and more specifically discussion on the production, isolation of *Bacillus sphaericus* and its formulated products has been covered. Some safety aspects of these biocides are also highlighted.

In recent years, more emphasis has been laid on the biotechnological approaches towards the development of biological agents as a substitute for chemical larvicides to control vectors of mosquitoes, viz. Culex, Aedes, Anophales, and Psorphora, Mansonia causing various human dreaded diseases (viz. Eastern, Western and Venezulian encephalitis, Japanese encephalitis, Murray Valley encephalitis, Yellow fever, Dengue, Californian encephalitis, Malaria, Filariasis, Vesicular Stomatitis, Wesselsbron disease, West Nile fever, Kyasanur Forest Disease, Diphasic meningo encephalitis, Leishmaniasis, Trypanosomiasis, Chagas disease, etc.). Amongst several types of micro- organisms,*Bacillus sphaericus* and *Bacillus thuringiensis* are developed and shown to possess a strong but specific mosquito larvicidal activity, and hence appear to be the most promising ones for mosquito control. Certain species of

B.sphaericus have been shown to be highly insecticidal to larvae of *Culex* spp. and *Anopheles* spp. These mosquito species are implicated as the important vector of malaria, filariasis, and encephalitis in tropical zones. The majority of the *Anopheles* species have their immature stages in various types of ground water, ranging from water- filled animal foot prints to running stream margins and the margins of lakes and marshes.

Production of *B.sphaericus* by Fermentation

Cultivation of *B.sphaericus* in a fermenter of 50 or 100 M^3 (batch process) containing medium, comprising carbon sources (molasses, dextrose, and sugar), nitrogen sources (cotton seed meal, fish meal, soyabean meal, and cotton seed oil) and essential trace elements (calcium, magnesium, phosphate, and sodium) under intense aeration and agitation for 20 to 24 h maintaining optimum pH (6.5 to 7.5) condition to achieve maximum sporulation and crystalline protoxin formation. Temperature, pH, dissolved oxygen, and oxygen uptake are monitored online using microprocessor attached automatic fermenters and manual measurement of dry weight, solids, residual glucose, nitrogen concentration, spore counts and colony forming units are also performed by drawing samples at different time intervals during fermentation (Fig.1). Spore crystal ratios are generally monitored during the final stages of fermentation in laboratory fermenters while scaling-up the process (Fig 2). The fermenter is harvested between 20 to 24h

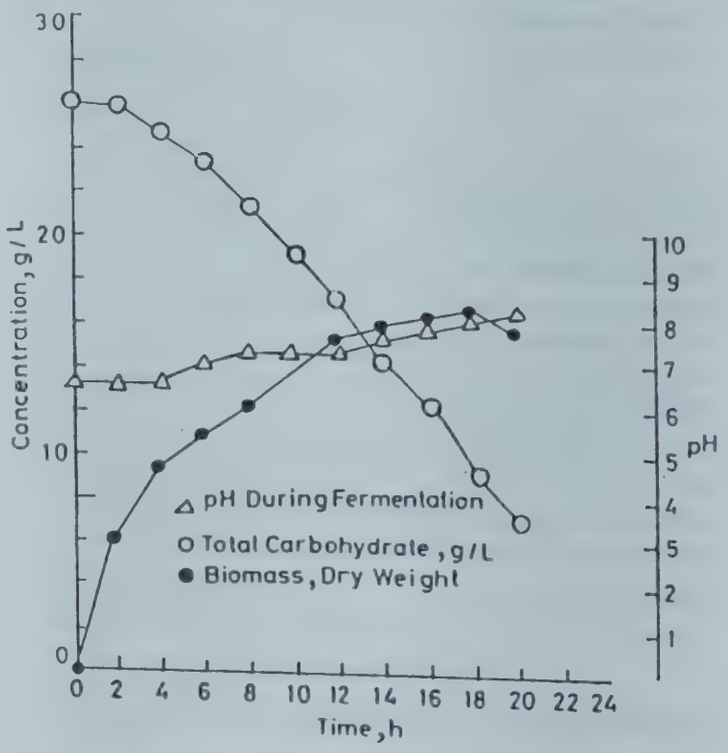


Fig. 1 — *Bacillus sphaericus* submerged fermentation (23 kL fermenter)

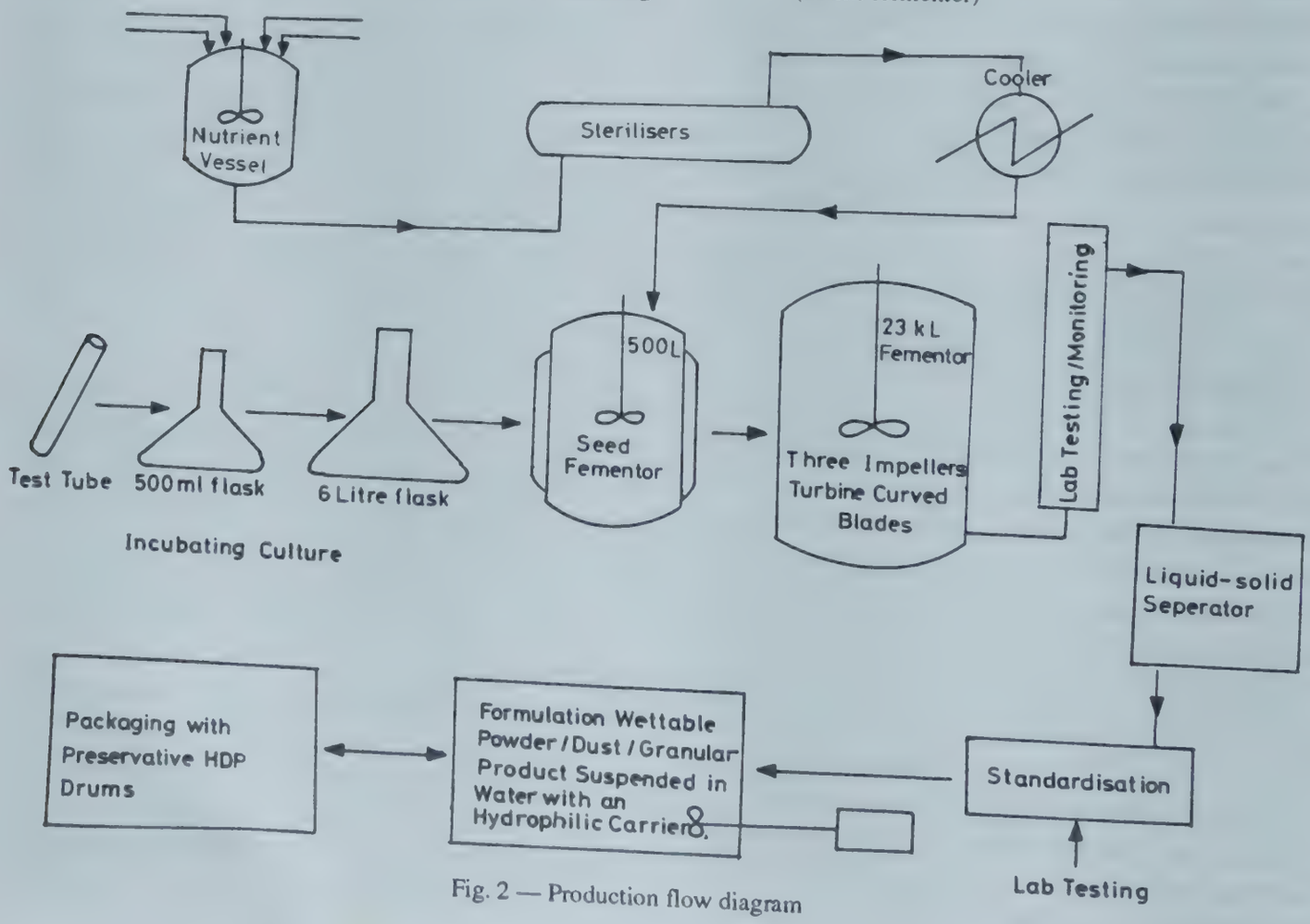


Fig. 2 — Production flow diagram

at pH more than 8.0 and potency is calculated using a set of ten-third instar larvae of mosquito species *Anopheles*, *Culex* and *Aedes*.

The larvicidal activity of *B.sphaericus* was found to be more against I and II instar larvae as compared to III and IV instars. Nearly 100 per cent mortality was observed between 48 to 72 h when treated in small water containers.

Isolation of Cell Biomass and Dosage Form Preparation

Isolation of biomass (cells) from the harvested fermentation broth is often difficult due to the low concentration of the products, their thermolabile nature, and poor stability. Often, it may be necessary to add stabilizing adjuvants immediately after harvesting to prevent spore death and/or germination.

The harvested broth (*B.sphaericus*) is processed through liquid- solid separator for cell concentration, by which product is concentrated from 2 to 3 per cent suspended solids between 15 to 20 per cent. After concentration (the spore slurry) it is formulated as a wettable powder, dust or granular product by suspending in aqueous media containing hydrophilic carrier. Other additives to aid adhesion or dispersion or attractants may be added if required prior to spraying.

Many industries have developed various formulations to circumvent field performance problems while spraying. The recent advancements in granular or pelleted formulation are directed toward achieving more uniform distribution on water surface and maintenance of particular concentration of *B.sphaericus* in the upper portion of the aquatic habitat, where there is a better chance of larval ingestion. Whereas, larger formulation are intended to float and provide for an extended release of *B.sphaericus* (may be for a few weeks) and thereby reducing the frequency of applications. Internationally available formulations of *B.thuringiensis* are : Abate 4E, Abate 2G, Bactimos G, Teknar G; Vectobal liquid; Bactimos wp; Bactimos Briquet; (E-emulsifiable concentrate; G-granule; wp-emulsifiable wettable powder). The material cost for larval control by ground application of dosage formulation of *B.sphaericus* (wp), *B.sphaericus*(G) is given in Table 1. The costing is approximate and was carried out based on material costs and other information available during 1993-94.

Table 1 — Material costs for larval control by ground application

Dosage formulation	Approximate lb/acre	Approximate cost* (Rs/acre)
B.sphaericus WP	12-15	275-300
B.sphaericus G	7-8	200-240

WP — Emulsible Wettable Powder, G — Granular Powder,
*— These figures were estimated during 1993-94

Safety Evaluation of *B.sphaericus*

Many non-target organisms like different species of fishes, frog tadpoles, mesocyclops, bugs, and gerris have been tested for toxicity of both *B.sphaericus* and *Bacillus thuringiensis* preparations. Both *Bacillus sphaericus* and *Bacillus thuringiensis* were found to be nontoxic (LC_{50} more than 1000 mg/L) to these organisms at concentrations required to kill vector larvae (*B.sphaericus* 0.05 to 2 mg/L, *Bacillus thruingiensis* 0.03 to 0.32 mg/L). Hence, fishes are compatible with biocides, which is important in integrated vector control approaches. *Bacillus sphaericus* is found to be non-mutagenic when tested by Ames and Chromansomal aberration tests. Even in acute inhalation toxicity test in rats, both these bacilli and their formulated products have not shown significant alterations in behavioural or body weight patterns and haematological parameters. A few limited experiments indicate that both these biocides appear to be harmless to higher mammals and non-target aquatic flora and fauna, thereby suggesting no adverse ecological effects during their use as biological tools for vector control. (Mahajan R C, Post graduate Institute for Medical Education and Research, Personal Communication).

Conclusion and Future Scope

There are various factors which affect the current and future acceptance of these biopesticides use in mosquito control. With documented chemical insecticide's resistance over 100 mosquito species worldover[12], bio-pesticides are welcome as an alternative to mosquito control agent. If their effectiveness can be guaranteed and their performance is dependable against mosquito control than the usage of biopesticides would further increase enormously.

The potential of the residual effectiveness of both *B.sphaericus* and *Bacillus thuringiensis* makes it very attractive under specific control situation. Although an advantage in the economy of these biocide usage and recycling may result in selective larval resistance mechanisms involving feeding behaviour and physiology[3]. Some workers have also pointed out that perhaps a greater selection pressure would produce a higher level of tolerance[13,14]. Mosquito resistance to synthetic insecticides[14] has challenged practical mosquito control world over and, therefore, the emergence of possible resistance to some biopesticides should always be remembered[15]. On account of this, additional mosquito species and strains should be studied. Certainly, the users of biopesticides hope that resistance to them does not develop as this presumption is purely derived from the experience of other agents like fungi and viruses. However, the acceptance of all biopesticides for practical mosquito control largely depends upon a complex interaction of factors, especially cost-effectiveness, and their *per se* effect on environmental safety and changing stage and federal regulations.

References

1 Lewis L C, *Biological Control*, In Ullman's Encyclopaedia of Industrial Chemistry, **Vol. A4**. (VCH Verlags of Sgesellschaft mbH, Germany) 1985, pp 77-97.

2 Miller L K, Lingg A J & Bulla L A (Jr), Bacterial, Viral and Fungal Insecticides, In *Biotechnology and Biological Frontiers*, edited by P H Abelson, (American Association for Advancement of Science, Washington, DC) 1984, pp 214-229.

3 Sutherland D J & Khoo B K, *J Ind Microbiol*, **28** (Suppl No.2) (1987) pp 55-60.

4 Sriram R, *Molecular Basis of Sporulation in Bacillus Studies on the Formation and Crystal Proteins of Bacillus thuringiensis var Israelensis*, Ph D Thesis, Anna University, Madras, 1987.

5 Kurstak F, *Microbial and Viral Pesticides* (Marcel Dekker, New York) 1982.

6 Barkay T, Chatterjee D, Cuskey S, Watter R, Genthren F & Bourquin A, Bacteria and the Environment. In *A revolution in Biotechnology*, edited by Marx J L (Cambridge University Press, New York) 1989, pp 94-102

7 Goldberg L J & Margalit J, A Bacterial Spore Demonstrating Rapid Larvicidal Activity Against *Anopheles sergentii, Uranotaenia unquiculata, Culex univattus,Aedes aegypti, Culex pipiens*, *Mosq News*, **41** (1977) pp 459-46.

8 Kellen W R & Clark T B, Lindgren J E, Ho B C, Rogoff M H & Singer S, *Bacillus sphaericus* Neide As A Pathogen of Mosquitoes, *J Invertebr Pathol*, 7 (1965) pp 442-448.

9 Payne J M & Davidson E W, Insecticidal Activity of the Crystalline Parasporal Inclusions and Other Components of *Bacillus sphaericus (1993) Spore Complex*, *J Invertebr Pathol*, **43** (1984) pp 383-388.

10 Jayaraman Kunthala, *Development of Bacillus sphaericus, by Fermentation and Evaluation of Its Mosquito Larvicidal Activity*, Anna university, Centre for Biotechnology, Madras 600 025 (Personal Communication, 1991).

11 Basu S K, *A New Biopesticide from Bacillus Origin*, (Personal communication, Central Drug Research Institute, Lucknow) 1991.

12 Brown A W A, Insecticide Resistance in Mosquitoes : A Pragmatic Review, *J Am Mosq Control Assoc*, **2** (1986) pp 123-140.

13 Gharib A H & Szälay-Marzso L, Selection for Resistance to *Bacillus thuringiensis* Serotype H-14 in Laboratory Strain of *Aedes aegypti* L,In *Fundamental and Applied Aspects in Invertebrate Pathology*, edited by R A Samson, J M Vlak and D Peters, *Proc Fourth Int Colloq Invertebr Pathol, Netherlands*, (1986) pp 37.

14 Goldman I F, Arnold J & Carlton B C, Selection for Resistance to *Bacillus thuringiensis* Subspecies Israelensis in Field and Laboratory Population of Mosquito *Aedes aegypti*, *J Invertebr Pathol*, **47** (1986) pp 317-324.

15 Bowman H G, Insect Responses to Microbial Infections, In *Microbial Control of Pests and Plant Diseases 1970-80*, edited by H D Burges (Academic Press, New York) 1986, pp 769-784.

Journal of Scientific & Industrial Research
Vol. 56, November 1997, pp 657 - 661

Salvadora persica — A Boon to Wasteland Development

S T Zodape* and V K Indusekhar

Central Salt & Marine Chemicals Research Institute, Bhavnagar 364 002, India

In the pursuit of using neglected resources, a new scientific concept of using wastelands has to be envisaged. The saline/alkaline lands are spread over nine million of ha in our country and are distributed both in inland and coastal regions. Such landscape can be profitably put to use by growing salt tolerant plants. *Salvadora persica* is one of the most promising plant to be grown on such lands. This plant can be grown on various soils and has immense industrial applications. The dried seeds contain 30 to 40 per cent oil which is of great economic significance. Purified oil is used in soap making and detergent industries as a substitute for coconut oil. The oil of *Salvadora* is being exploited by various companies like, Godrej Soaps Ltd., Mumbai; Tata Oil Mills, Mumbai; Hindustan Lever Ltd., Mumbai; etc. The root of this plant contains a steam distillable oil that has 90 per cent benzylisothiocyanate, the compound responsible for decreasing dental caries and hence can be used in the preparation of tooth paste. The wood of this plant is useful in the timber industry. Apart from this, the plant has various uses like in medicinal component, useful as a shelter belt, fuel, and fodder. This paper aims at elucidating the utilization of wastelands by growing *Salvadora persica* which has various immense potential applications in the above fields.

Introduction

Soil is one of the renewable sources and finds a very important role in influencing the life cycle and pattern of humans. An increase in demand of natural products decreases the soil productivity because of over exploitation and ineffective management. Gradually the soil is turned as wasteland meaning thereby unproductive requiring lot of efforts for bringing it back to normalcy. The term wasteland should not be taken by word and the soil should not be discarded[1].

The wasteland in the country accounts for approximately 160 million ha comprising forest, saline/alkaline regions, ravines and gullies, sand dunes, wind and water eroded areas and water logged areas. The saline/alkaline wastelands constitute over nine million ha and are distributed both in inland and in coastal regions. Gujarat has wasteland covering approximately six to seven million ha[2]. Salt affected soils alone are estimated to spread over an area of 15 lakh ha in Gujarat State[3]. Such soils can be profitably put to use by growing salt tolerant plants[4]. One of the promising plant to be grown on such soils is *Salvadora persica*[5,6]. Experiments on this species on salt affected black soils are under progress[4].

Salvadora can grow above 300 meter altitude besides rocky and marshy areas which are suitable for it to grow. It can also grow on saline as well as non-saline wasteland, eroded land and marginal land having texture in the range of sandy to silty clay soils. The species tolerates salinity up to 50 dSm^{-1} and *p*H value between 6.0 to 8.5, highly drought and salt tolerant and thrives at 10 to 45°C. It is suitable for arid and semi-arid conditions, but can also be grown under sub-humid conditions. *Salvadora* can be cultivated in the region receiving annual rainfall from 200 mm to 1000 mm[7]. It also grows on sea coast under spray zone[5].

The plant is useful as fodder, medicinal ingredient, tooth brush, food and fuel, etc., and oil from seeds is an excellent raw material for soap and detergent industry as a substitute for coconut oil.

Biological Aspects

Botany of the Plant — Genus *Salvadora* belongs to a family Salvadoraceae which represents five species out of which *S. oleoides* and *S. persica* are

* Author for correspondence

available in India. *S. persica* is widely distributed in Gujarat, Rajasthan, Haryana, Punjab and to some extent in Andhra Pradesh, Karnataka and Tamil Nadu[5]. It is also distributed in tropical Africa and Asia, extending to Egypt, Mascarene Island and China[8]. Its distribution is also reported in Middle East, Saudi Arabia[9], Eastern Africa, Arabia, Syria, and Sri Lanka[10].

Salvadora persica is an evergreen shrub or a small tree to medium sized tree with numerous drooping young branches[11]. The leaves vary in shape, elliptic-ovate or ovate-lanceolate, somewhat fleshy. Flowers pedicellate are greenish white or greenish yellow in lax panicles[8]. Flowering occurs during November-December and fruits ripe during March[5]. However the flowering is reported from October to February and ripening of fruits somewhere in April to June[11]. Fruits are globose or round, smooth, red when ripe[8].

Cultivation Practices

The tree readily propagates from seeds and coppices, but the growth is slow. For planting purposes three-year old seedlings from nursery are necessary[8]. It has also been suggested that 5 to 6 month or one-year old seedlings can be transplanted in the fields[5]. This plant can be propagated not only by seeds but also from root and shoot suckers. Seeds are small having about 3 to 4 mm diam. The weight of 1000 seeds is nearly 50 gm[6].

The seedlings are raised in polythene bags having a desired proportion of soil, sand, farm yard manure (FYM), di-ammonium phosphate (DAP) and furadan. Prior to sowing, seeds are soaked in water for 24 h and the pulp is removed by gentle pressing. Generally, six month old seedlings are transferred in the field after the onset of monsoon which ensures sufficient soil moisture. Nearly 400 to 500 seedlings are planted in one ha wasteland. A spacing of 5 x 5 meter would result in 400 plants/ha[6]. The spacing may vary from location to location. The planting of 500 plants/ha has been reported by Shah[3].

Micropropagation — There are several distinct advantages in commercial production of plants by this technique over conventional methods such as rapid multiplication, speedy release of varieties with improved phenotypes, maintaining clonal and phenotypic uniformity among offsprings, yield in large numbers that too in small space, round the year production and diseased indexed plants making easier international exchange. Micro- propagation industry is, in fact, one of the recognised profit making option. In 1994,there were about 21 commercial plant micro-propagation units in production with targeted annual production capacity of 80 million plants. Godrej Plant Biotech Ltd (earlier the Unicorn Biotek, Hyderabad) is a commercial unit for the micro-propagation of *Salvadora*[12].

Work Done at CSMCRI, Bhavnagar

A systematic work on this plant has been done and is being carried out in this Institute, having a highly skilled group working in the area of bio-salinity mainly dealing with the development of wasteland. A systematic survey work was carried out and the seeds were collected from the selected plants from the nature. Further work on method of development of germination and raising the nursery has been successfully carried out. It has emerged as a promis-

Dr S T Zodape did his PhD in Botany. He is presently working as Scientist 'C' at Central Salt and Marine Chemicals Research Institute, Bhavnagar. He has wide experience on the Methods of Propagation, Plant and Soil Analysis, Culture of Marine Algae, its nutritional studies, Eco-physiology of Cotton, etc. He has ten papers to his credit, published in national and international journals.

Dr V K Indusekhar was born on 16 September 1937. He is presently working as Scientist 'F' at Central Salt & Marine Chemicals Research Institute, Bhavnagar. He had worked in National Chemical Laboratory, Pune from 1958 to 1966. Since then, he is engaged in Research activities in Central Salt and Marine Chemicals Research Institute, Bhavnagar. He has very wide experience in ion-exchange technology, membrane separation technology employing electro-dialysis. He has carried out various schemes for the treatment of brackish water to potable water, seawater desalination by electro-dialysis, effluent treatment and chemical recovery from industrial process water. He has also carried out deashing of sugarcane juice to get enhanced yield of sugar crystals and quality molasses. He has 70 papers to his credit, published in national and international journals, six patents, and three awards.

ing agrotechnology for cultivation of *Salvadora persica*, which is released to the interested parties on advisory consultancy basis. The tissue culture technique is also developed for micro-propagation of *Salvadora*, the field trials of which are in progress.

So far the Institute has given the advisory consultancy to a few parties.

Post Planting Operation

The plant gets established within 15 to 20 d. For conservation of water, a saucer of 1 meter diam may be prepared around the plant.

Irrigation is the most important requirement after transplantation, the frequency of which is largely dependent upon the local conditions. Fortunately, for *Salvadora* quality of irrigation water is not very critical[16]. Initially 18 normal water irrigations are given for the first year. Subsequently saline water irrigation is given without affecting the growth[3].

Irrigations are given depending upon the water holding capacity of the soil. In a month, two to three irrigations for the first three months, followed by one to two irrigations per month, up to 2 y, may be applied for better establishment and growth. During flowering (November, December, and January) and fruiting period, in a month, one irrigation will suffice flowering, fruiting, and seed yield[7].

The CSMCRI[7] has recommended the doses of fertilizers up to 5 y. The suggested fertilizers are DAP, urea, and muriate of potash to be applied in increasing quantity with the progress of the plantation. The use of fertilizers is also recommended by Shah[3] and Vyas and Mistry[6].

It has been reported that *Salvadora* is infected by leaf defoliating larvae which can easily be controlled by recommended insecticides[6]. Many fungi such as *Cercospora udaipurensis*, *Placosoma salvdorae* and *Septogloeum salvadorae* have been reported for the first time, damaging the leaves from Rajasthan[8]. During winter sporadic instances of leaf and stem galls were recorded but it can be brought under control by soil application of furadan and foliar application of Rogor 36 EC. Some times, during cloudy weather leaf eating worms, Aphids and Jasids are noticed which can be controlled by foliar spraying of any contact poison insecticides[7].

Uses of *Salvadora*

Chewing sticks are believed to contain chemical substances which inhibit plaque formation and gingivitis. A tooth paste made from *Salvadora persica* is available for use to the masses. The stick contains a chemical having action equivalent to that of chlorohexidine gluconate which is known as an antiplaque agent[13]. Chewing sticks obtained from the roots and canes of some plants such as *Salvadora persica* growing in arid areas of East Africa and South Asia are known to have antibacterial properties which is used by local population. Some studies have shown that the users of such natural tooth brushes have significantly good dental health[14]. Similar reports of using *Salvadora persica* root as a brushing stick for cleaning teeth in many parts of the world have been reported[15,16,9].

Chemicals — Dried seeds contain 30 to 40 per cent nonedible oil, with 30 per cent lauric and 50 per cent myristic acid which is used for soap making and detergent preparation as a substitute to coconut oil. The oil of *Salvadora* is being exploited by various companies like Godrej Soaps Ltd, Bombay, Tata Oil Mills, Hindustan Lever Ltd, Aegis Chemicals, Lauric Oils/Seeds and Seedlings, and KVIC, Bombay[5]. The use of oil in soap and detergent industry has been reported by Rao *et al.*[4] Kamal *et al.*[17] have isolated five glycosides from the stems of *Salvadora persica* which are sodium 1-O-benzyl-β-D- glucopyranoside-2- sulphate(salvadoside)and 5,5′-dimethoxylariciresinol, 4,4′- bis-O-β-D- glucopyranoside (*Salvadora*side), syringin, liriodendrin, and sitosterol 3-O- glucopyranoside. Leaves of *Salvadora persica* contain a flavonoid quarecetin and many phenolic acids like vanillic, syringic, ferulic and *p*-hydroxy benzoic acid and salicylic acid[11]. The stick of *Salvadora persica* species showed several unique nitrogen containing compounds, some of which were tentatively identified as pyrrolidine, pyrrole and piperidine derivatives on the basis of their mass spectra and chromatographic elution order[14].

Antifungal, Antibacterial and Antiviral Substances

Benzylisothiocynate (BIT) is naturally occurring compound in plant tissues. The root of *Salvadora persica* contains a steam distillable oil, composed of 10 per cent benzylnitrate and 90 per cent benzylisothiocyanate. This compound is found to inhibit

growth of acid production of *Streptococcus mutans*, the growth and acid production of which is responsible for dental caries/dental plaque. The study suggests that BIT might be useful in decreasing the incidence of dental caries. It has been suggested that enzyme inhibitor such as BIT might be introduced into tooth paste. Some vegetables such as cabbage, brussels sprouts, and cauliflower also contain BIT[15]. The chemical analysis of miswak (root of *Salvadora persica*) extracts showed that it contained chlorine, trimethylamine, an alkaloid, resin, silica, vitamin C, sulphur, and tannins which may be responsible for the antibacterial and antifungal activities of the chewing stick[9]. The presence of trimethylamine, small amount of resins, colouring matter and traces of tannins, and saponins has been reported in Wealth of India[8].

Al-Bageih[16] has reported the virucidal activity of BIT. Herpes simplex virus (HSV) is one of the most prevalent and communicable infectious viruses found in humans. Herpes simplex virus type-1 (HSV-1) is most frequently the cause of gingivostomatitis, recurrent herpes labialis, herpes encephalitis, skin infections, and conjunctiva. The virucidal activity of BIT against herpes simplex virus type-1 found by Al-Bageih[16] seems to support the use of miswak as preventive measure in controlling oral infections.

Medicinal Uses — The ethanolic extract of *Salvadora persica* is commonly used in traditional Arab systems of medicine which was tested for its cytological effects on bone marrow cells of mice[18].

Al Said Mansour[19] has given an account of the use of this plant in Saudi traditional medicine along with its main chemical constituents. This study is not only to document the current status of traditional uses of medicinal plants in Saudi Arabia, but also to make one aware of possible new drug resources. The leaves are found to have wide applications in the field of medicine for healing of wounds, swollen joints and inflamed glands, as an antidote to all sorts of poison, in the establishment of pregnancy, and against cough, and scurvy[11]. It has been reported in Wealth of India that the leaves also possess anti-scorbutic and astringent properties. A decoction of the leaves is used for asthma and cough, and a poultice made out of them is applied to painful tumours and piles. They are also used as an external application for rheumatism. Dried leaves in small doses are given with copious amount of water for treatment of flatulent dyspepsia. The bark of stem is used as an ascarifuge for gastric troubles. The decoction of stem bark is used as tonic and stimulant in low fevers and as an emmenagogue.

The sweet edible fruits are carminative, diuretic, and lithotrophic having stomachic properties[11], and are used in biliousness and rheumatism[8].

Seeds have a bitter sharp taste. They are considered purgative, diuretic and tonic, oil of seed is applied to the skin for rheumatism[8]. Nonedible oil of *Salvadora persica* at 5 ml/kg of wheat seeds has shown significant improvement in the control for protecting the grains from pest infestation[20].

Fodder — The plant is used as feedstuff for domestic animals[4,21,22]. The leaves of *Salvadora persica* contain 8.2 to 16 per cent protein which indicate that it is a dependable forage substitute in regions where no other forage species can grow. Only green and young leaves should be used as forage as the old leaves contain high amount of salts[23]. The leaves can also be used as fodder for Camel[8].

Food — Consumption of fruit of *Salvadora persica* has been observed amongst the Allaqui nomads[22]. A fermented drink is reported to be made from the edible fruits. The leaves are eaten as vegetable in eastern tropical Africa and are used in the preparation of sauce. The tender shoots and leaves are eaten as salad[8].

Fuel — The stem of *Salvadora* provides firewood[4,11,22].

Shelter Belts — The tree is suitable for growing in shelter belts and as windbreaker for protecting the farm habitations, gardens, orchards, etc.[8]

Wood — Wood is soft, white, easy to work and can be easily polished. It is not liable to be attacked by termites, and is used by Egyptians for Coffins[8]. The plant is also used for timber by nomads in Allaqui[22].

Soil Binder — The tree is an excellent soil binder, arrests advance of desert and improves ecology from commercial point of view[3].

Our Government is concerned about the wasteland and is taking some measures for sustained development of non-forest/private wasteland. It is also assisting non-government organisations (NGOs) and is encouraging people's participation in wasteland development. A task-force for wasteland develop-

ment and investment promotion council is being finalised. The principal objective is to channelise and mobilize resources from financial institutions, corporate bodies including user industries and other entrepreneurs for development of wasteland belonging to individual farmers, villages, institutions, and government agencies.

Salvadora persica is an excellent plant for sustained development of wasteland particularly salt affected with multiple effects, economical and ecological. Therefore, all those who are concerned in improving ecology will do good if they initiate propagation of *Salvadora persica* from commercial point of view. This activity will also supplement the efforts of the government and add one more oilseed to the currently available ones[3].

The cultivation of *Salvadora persica* on saline land is supported by National Bank for Agriculture and Rural Development (NABARD).

Acknowledgement

The authors are grateful to Prof. P Natarajan, Dr S D Gomkale and scientists of Phytosalinity Discipline for their help.

References

1 Srivastava A K, Strategy for Wasteland Afforestation in Gujarat, *Indian Forest*, **118** (1992) pp 623-629.

2 Workshop on *Desert Economic Plants and Halophytes for Coastal Wasteland Development-Retrospects and Prospects*, held at Central Salt & Marine Chemicals Research Institute, Bhavnagar, 1995.

3 Shah C D, Experience of Growing *Salvadora persica* on Highly Saline Soil, Paper presented at the Workshop on *Desert Economic Plants and Halophytes for Coastal Wasteland Development- Retrospect and Prospects* held at Central Salt & Marine Chemicals Research Institute, Bhavnagar, 1995.

4 Gururaja Rao G, Singh R & Bhargava G P, Species Diversity on Salt Affected Soils Under Canal Command Areas and in Bhal Regions in Gujarat State, *Indian Forest*, **121** (1995) pp 1143-46.

5 Note on *Salvadora*, Central Salt and Marine Chemicals, Research Institute, Bhavnagar.

6 Vyas B N & Mistry K B, Agronomic Practices for *Jatropha*, *Salvadora* and *Jojoba* Plantations. Paper presented at the Seminar on *Developments in Vegetable oil Industry*, organised by Oil Technologies Association of India, held at Bombay, 1993.

7 *Silviculture Practices to be Followed for the Raising of Plantation of* Salvadora persica, Central Salt and Marine Chemicals Research Institute, Bhavnagar.

8 *The Wealth of India Raw Materials* (Publications and Information Directorate, CSIR, New Delhi) **Vol.9** (1988) pp 194-195.

9 Al-Bagieh N H, Idowu A & Salako N O, Effect of Aqueous Extract of Miswak on the *in vitro* Growth of *Candida albicans*, *Microbios*, **80** (1994) pp 107-113.

10 Hooker J D, *Flora of British India*, (Published under the authority of the Secretary of State for Indian Council, **Vol.3** (1882) pp 619.

11 Krishnakumar M, *Studies on Salt Tolerant and Utility Aspects of Salvadora persica*, Ph D Thesis, Bhavnagar University, Bhavnagar, 1986.

12 Govil S & Gupta S C, Plant Micro-propagation Industry in India :Retrospects and Prospects, *J Sci Ind Res*, **53** (1994) pp 768-77.

13 Gazi M A, Lambourne A & Chagla A H, The Anti-plaque Effect of Tooth Paste Containing *Salvadora persica* Compared with Cyclohexidine Gluconate, *Clin Prevent Dent*, **9** (1987) pp 3-8.

14 Galletti G C,Chiavari G & Kahie Y D, Pyrolysis/Gas chromatography/Ion-trap Mass Spectrometry of 'Tooth Brush' Tree (*Salvadora persica* L.), *Rapid Commun Mass Spectrum*, **7** (1993) pp 651-55.

15 Al-Bageih N H & Weinberg E D, Benzylisothiocyanate — A Possible Agent for Controlling Dental Caries, *Microbios Lett*, **39** (1988) pp 143-51.

16 Al-Bagieh N H, Anti-herpes Simplex Virus Type-1 Activity of Benzylisothiocyanate, *Biomed Lett*, **47** (1992) pp 67-70.

17 Kamal M S, Ohtani K, Assaf M H, Rassai R, El-Shanwani M A, Yamasaki K, Ali A A & Tanaka O, Lignan Glycosides from Stems of *Salvadora persica*, *Fhytochem (O)*, **31** (1992) pp 2469-71.

18 Shah A H, Tariq M, Ageel A M & Qureshi S, Cytological Studies on Some Plants Used in Traditional Arab Medicine, *Fitoteripia*, **60** (1989) pp 171-173.

19 Al-Said M S, Traditional Medicinal Plants of Saudi Arabia, Am *J Chin Med*, **21** (1993) pp 291-98.

20 Gupta H C, Verma T P, Bareth S S & Mathur B N, Evaluation of Some Nonedible Oils as Grain Protectant in Wheat and Their Subsequent Effect on Germination, *Indian J Entomol*, **50** (1989) pp 147-50.

21 Faye A, Kamil M & Labonne M, Trace Elements in Feedstuff and Blood Plasma of Ruminants in Djibouti, *Rev Elev Med Vet Pays Trop*, **43** (1990) pp 372-73.

22 Belal A E & Springuel I, Economic Value of Plant Diversity in Arid Environments, *Nature Resour*, **32** (1996) pp 33-39.

23 Joshi A J, Krishnakumar M & Mali B S, Seasonal Changes in Proteins, Amino Acids and Minerals in *Salvadora persica* with Reference to Saline Habitats, *Indian J Plant Physiol*, **36** (1993) pp 202-204.

Journal of Scientific & Industrial Research
Vol. 56, November 1997, pp 662 - 672

Fluid CO_2 Extraction and Hydrodistillation of Certain Biocidal Essential Oils and Their Constituents

Padma Vasudevan, Mamta Tandon and Namrata Pathak

Centre for Rural Development and Technology, Indian Institute of Technology, New Delhi 110016, India

and

Peter Nuennerich, Frank Mueller, Altin Mele and Harro Lentz

Universitaet Siegen, Fachbereich Chemie, 57068, Siegen, Germany

Received: 28 April 1997; accepted: 18 August 1997

Natural products, traditionally used as biocides in indigenous cultures, are being reevaluated for safer means of bacterial and pest control, as compared to the synthetics. While unequivocal identification of bioactive components of plant extracts is difficult due to synergy and other type of interactions among the constituents, a variety of terpenoids in the essential oils have been shown to be bioactive. The qualitative and quantitative composition of the extracts vary depending upon the extraction conditions. In this article, studies on four common herbs *Murraya koenigii*, *Lantana camara*, *Ocimum sanctum* and *Tagetes patula* are presented.These herbs were extracted by liquid CO_2 (subcritical liquid extract; SLE), supercritical fluid CO_2 (supercritical fluid extract; SFE) and hydrodistillation. The components extracted were characterized by TLC, GC and GC/MS.

Introduction

In traditional systems, some natural products are used as insecticides, bacteriocides, fungicides and pharmaceuticals. With many of the synthetic insecticides being removed from the markets because of their harmful effects on the environment and ineffectiveness due to development of insect resistance, scientists are again turning towards natural products for safer alternatives[1,2]. Reports are available on the bioactivity of essential oils from specific genus and species of plants of a region or family. In this context, the families of Compositeae[3], Labiateae[4,5] and Rutaceae are well known. Many of these have been traditionally used as foods and flavourants and have simultaneously extended the benefits of their biocidal and medicinal properties. The bioactive components of these oils have not been often fully identified and synergetic effects have been noted among the constituents. Some of the terpenoids[6-15] present in many essential oils and active against different microorganisms, are eugenol, isoeugenol, linalool, pinenes, limonene, cineol and citral. From the *Ocimum* sp., the biocidal activity of eugenol and methyl eugenol against four bacterial and six fungal cultures was reported by Dey and Choudhuri[16], while caryophyllene lacked such activity. Methyl cinnamate and methyl chavicol from *Ocimum basilicum* were reported for their insecticidal action by Deshpande[17]. *Ocimum suave* leaves and *Eugenea caryophyllate* cloves are used as grain protectants in different parts of the African continent[18]. Cinnamaldehyde and eugenol have been reported to be active against wood destroying fung[19]. Eugenol acetate and geraniol acetate have been found to be active against keratinophilic fungi. Eugenol and isoeugenol have been reported to be effective against *Candida albicans in vivo*[20]. As for the extracts of Compositeae, the potency of pyrethrum is well known. Thiophene compounds from the *Tagetes* sp. have been studied extensively for their nematocidal value. (5E)-Ocimene, isolated from *T. minuta* flowers and leaves, is reported to be active against mosquito larvae[21-23]

* Author for correspoondence

The quantity of various constituents present in a plant depends not only on its species, chemotypes, variants, soil, climate, nutrient inputs, plant part and stage of maturity, but also on the conditions of extraction. These include conditions like mode of drying, level of crushing, nature of solvent, temperature and pressure of extraction. Since the extract is generally a complex mixture of the aromatic volatiles with resins, including fatty oils and pigments such as flavanoids and carotenoids, the yield or quantity has to be balanced delicately with the quality by maximizing the desired products through optimisation of the conditions of extraction.

Steam distillation, a time-tested technique for extraction, may sometimes lead to degradation of such products which are thermally labile or hydrolysable. In solvent extraction technique, the residual solvent in the product may be unacceptable. Recently, fluid CO_2 has come up as an alternative for low temperature extraction, without the fear of thermal degradation and solvent contamination, and the extracts are acceptable even in food and pharmaceuticals. The conditions in fluid CO_2 extractions can be adjusted for obtaining high quality products. In this article, studies on four tropical herbs, viz. *Murraya koenigii*, *Lantana camara*, *Ocimum sanctum*, and *Tagetes patula*, known for the bioactivity of their essential oils have been presented. The products from the fluid CO_2 extractions have been compared with those obtained through hydrodistillation and solvent extraction.

***Murraya koenigii* L.**

The leaves of this plant are being widely used in Indian cookery for centuries and are popularly referred to as curry leaves[24]. The intensely aromatic leaves from the small tree are best to use when fresh. In view of the loss of aroma from the leaves on storage, the oil is extracted and stored. Earlier workers have reported the composition of essential oil extracted from these leaves by steam distillation and solvent extraction[25-27]. In this paper, results of fluid CO_2 extraction are presented and the oil composition has been compared with that of the extracts obtained by conventional methods.

Lantana camara

Lantana species, a flowery ornamental plant, is now spreading as a weed in tropical countries like India. Being hepatotoxic to animals, there has been concern for its control. Instead of using weedicides and other intensive methods resulting in impairment of environment, its biomass can be profitably used if phytochemical extraction from these plants become economically viable. Continuous harvesting of these plants will keep their proliferation under control. Earlier, Vasudevan and Gujral[28] have pointed out its potential applications. The bio-active components could be processed into appropriate formulations. In light of this, the essential oil of *Lantana camara* was extracted and examined.

Ocimum sanctum

Ocimum popularly known as basil, is a genus of aromatic shrub distributed all over the world. *Ocimum basilicum* is a food flavourant. *Ocimum sanctum* is a sacred plant which is worshipped since vedic times and its extracts are used as a home remedy. Reports are available on the extraction of its essential oil by hydrodistillation and solvent extraction, and also on the oil composition and its bioactivity[16]. As for fluid CO_2 extraction, only one research note[29] seems to have been published on the supercritical CO_2 extract of *Ocimum basilicum*. In the present study, results of liquid CO_2 extraction of *Ocimum sanctum* are reported.

Tagetes patula

Tagetes is a genus of herbs commonly known as marigold. It is native of Mexico but has been naturalized in tropics and sub- tropics. Several ornamental species are available. However, in some parts of the world, for example in India, this plant is grown as a crop, as its flower heads find a good market. Most *Tagetes* species yield strong aromatic essential oil. The oil extracted from leaf and the tender ones are reported to be richest in essential oil[30]. The oil is commonly obtained by steam distillation and a number of workers have reported the terpenoid composition of the oil, which varies from species to species[31,32]

Literature survey has shown that there are only two papers on the supercritical CO_2 extraction of *Tagetes*[33,34] but no reference is available on the liquid CO_2 extraction. Recently, interest has been evoked on its insecticidal activity. This as well as other applications of the plant have been reviewed by Vasudevan *et al.*[35].

Experimental

Fluid CO_2 extraction was carried out by two methods, viz. liquid CO_2 soxhlet extraction at 15-20°C at pressures around 50-55 bar over durations of 1 to 8 h and supercritical fluid extraction around 40°C at pressures around 250-300 bar. The details of apparatus and procedures are described elsewhere[36,37]. A Hewlett Packard Gas Chromatograph (GC) HP5890, was used for analysing the volatiles under conditions described below.

Column Type : Quartz glass capillary column HP5 (25m x 0.20mm) (cross-linked diphenyl dimethyl silicon gum with 5% phenyl, split 100:1); Injection Temperature : 200°C; Column Temperature : 70°C held 2 min; Heated at the rate of 10°C per minute for 18 min to 250°C and held for 6 to 20 min; Carrier gas: Nitrogen; Detector Type : FID; Detector Temperature: 200°C; Sample Size : 0.2 μL, Split : 1 : 100.

A Hewlett Packard Mass spectrometer (GC/MS) system 5988 was used. The ionizing energy was 70ev. The column was HP-1 (cross-linked dimethyl silicone gum) 12m × 0.2mm × 0.33 μm film thickness.

Thin layer chromatography (TLC) was used for the detection of terpenoids and fatty oils as per details given below[37-39]. For terpenoids, Millar and Kirchner[39] noted that Rf values can serve as means of distinguishing hydrocarbons from non-hydrocarbons. Hydrocarbons have appreciable Rf values with hexane as solvent whereas Rf value for non-hydrocarbons is zero.

TLC was done using toluene : ethyl acetate mixture (93 : 7) as per procedure described by Wagner *et al.*[38], Adsorbent : Silicagel 60 F_{254} pre-coated TLC plate (Merck); Reagent for detection : Vanillin+Sulphuric acid, followed by heating at 100°C for 10 min; Characteristic spots developed for different terpenoids. For TLC with n-hexane and n-heptane, the solvent was distilled over sodium and TLC plates were dried for two days at 130°C and cooled down over silica gel. Rf values were determined both for standard and plant extracts.

Rf values of standard compounds β-pinene, linalool, limonene, ocimene, and β-caryophyllene were measured experimentally for comparison with those obtained from plant extracts.

Results and Discussion

The data for the plants *Murraya koenigii*, *Lantana camara*, *Ocimum sanctum* and *Tagetes patula*, are presented along with the conclusions for each plant under extraction conditions for different components.

Murraya koenigii

The leaves were selected from 2 different trees of about 10 years of age and the samples were harvested in Nov.'95 and Feb.'96. The samples were dried and used for extraction as such and after crushing. The duration of extraction was also varied. The yields under different conditions from different sample lots are given in Table 1. TLC of hydrodistillate of *M. koenigii* showed the presence of limonene, linalool, β-pinene, ocimene and β-caryophylene; SLE showed the presence of limonene, linalool, pinene and β-

Table 1 — Fluid CO_2 extraction condition and yield of *Murraya koenigii*

Sl. No.	Extraction method	Harvest date	Leaf weight (dried), g	CO_2 used	Pressure bar	Temp °C	Time h	No.of cycles	Yield %
1	SLE	Dec.'95 crushed	20	192	52	15-17	2.0	10	1.0
2	SLE	Feb.'96 crushed	160	187	55-57	18-20	3.5	30	2.6
3	SFE	Feb.'96 crushed	120	5000	300	40	1.0	—	1.6

SLE : Subcritical liquid extract
SFE : Supercritical fluid extract

caryophylene; SFE showed only β-caryophylene whereas $CHCl_3$ extract showed the presence of linalool, pinene and β-caryophylene. In Table 2, the retention time (RT) of GC peaks and the identification of the components in terms of standard RT and/or MS are presented. In liquid CO_2 extraction, the yields went up from 1% to 2.6% as the duration

Table 2 — Components of *Murraya koenigii* oil

Sl. No	Component	Hydrodistillate				SLE		$CHCl_3$ Extract	
		GC-MS		GC		GC		GC	
		RT	Rel. %	RT	Rel.%	RT	Rel.%	RT	Rel.%
1.	Thujene/Sabinene	8.30	4.12	8.70	7.9	9.07	0.68	—	—
2.	Unidentified	—	—	9.20	0.24	9.20	2.21	—	—
3.	α-Pinene	9.49	0.26	9.50	2.5	9.33	1.26		
4.	β-Pinene	—	—	9.60	0.77	9.61	1.01	—	—
5.	α-Phellandrene	—	—	10.06	0.36	—	—	—	—
6.	Limonene	—	—	10.52	0.84	10.49	0.77	—	—
7.	β-Phellandrene	10.51	2.57	10.58	3.75	—	—	10.56	2.84
8.	Trans ocimene	10.73	3.12	10.69	3.12	—	—	—	—
9.	Linalool	11.80	0.27	11.68	0.58	—	—	12.84	2.06
10.	Unidentified	—	—	14.88	0.25	—	—	13.23	11.80
11.	Unidentified	15.12	0.22	—	—	—	—	—	—
12.	Elemene	16.89	0.18	16.92	0.73	—	—	—	—
13.	Unidentified	17.03	0.84	—	—	—	—	—	—
14.	Unidentified	17.43	0.22	17.51	0.22	17.51	1.77	—	—
15.	β-Caryophyllene	17.78	35.80	17.57	43.10	17.57	45.80	17.48	27.80
16.	Gujunene	17.96	1.46	17.86	1.31	17.86	2.50	—	—
17.	α-Caryophyllene	18.18	9.17	18.08	8.19	18.08	8.26	18.00	5.13
18.	α-Copaene	18.36	1.46	18.28	0.87	18.28	1.33	—	—
19.	ε-Murrolene	—	—	18.51	0.75	18.51	1.67	—	—
20.	Cadinene	18.67	8.43	18.57	5.16	18.57	7.80	18.48	5.30
21.	Selinene	18.76	8.88	18.66	8.90	18.66	15.30	18.58	8.56
22.	α-Cubebene	18.9	0.52	18.87	0.36	18.87	0.61	—	—
23.	Unidentified	19.07	0.39	19.00	0.24	—	—	—	—
24.	β-Farnesene	—	—	19.13	0.53	—	—	—	—
25.	Citronellol	19.25	0.78	—	—	—	—	—	—
26.	Geraniol	19.56	0.38	—	—	—	—	—	—
27.	β-Bisabolene	19.65	0.61	19.63	0.39	—	—	—	—
28.	Geranyl acetate	—	—	19.87	0.85	—	—	—	—
29.	Bornylacetate	20.05	7.81	20.02	3.79	20.02	1.23	19.93	4.18
30.	Unidentified	20.18	1.02	20.20	0.51	—	—	—	—
31.	Nerol Acetate	20.36	4.61	20.37	1.88	20.37	0.64	20.28	2.51
32.	Unidentified	—	—	20.47	0.90	—	—	—	—
33.	Citronellol acetate	20.62	1.36	—	—	—	—	—	—

of extraction increased. SFE at 300 bar at 40°C gave 2% yield. However, with increase in the duration and pressure of extraction, the colour of the product deepened from light yellow and finally became dark green and in the SFE product, considerable amount of resin was present. In contrast, the hydrodistillate was colourless and retained the pleasant aroma. But, the leaf samples on hydrodistillation without crushing yielded only 0.3% volatile oil on dry weight basis, in 6 h (Table 1).

In a study using steam distillation and solvent extraction techniques, Prakash and Natarajan[26] extracted tender as well as mature leaves after drying by various methods to 4.5-7% moisture content. A maximum of 0.8% oil was obtained by the steam distillation of tender leaves. As compared to fresh leaves, dried leaves gave better yields, indicating the role played by the moisture in the release of oil. The yields from mature leaves with 65-70% moisture content was only 0.35%. Use of various solvents gave higher yields as non-volatiles also get extracted.

Oil Composition

β-Caryophyllene was identified as the major component with significant amounts of thujene, α-caryophyllene and phellandrene (Table 2). While almost all the earlier workers have reported β-caryophyllene as the major component, the data regarding other components vary. β- Gurjunene, elemene and phellandrene are associated with the aroma[27]. Quantitative separation by chromatography was effected by Nigam and Purohit[25] for the constituents α- and β-pinene, sabinene dipentene, cadinene and terpeniol. In this study, the presence of sesquiterpene alcohols and acetates was recognized. It may be noted that hydrodistillate from tender leaves of another plant has several additional components like eugenol and linalool. Thus, plant to plant and seasonal variations have also been noted.

The major components obtained from the liquid CO_2 extracts are the same as with hydrodistillates; β-caryophyllene and α-caryophyllene being dominant. However, large amounts of components possibly esters, coloured compounds and resins are also extracted by liquid CO_2 at longer durations. Solvent-extraction with chloroform also yielded β- caryophyllene as the dominant compound along with coloured compounds.

Due to the presence of large amounts of resinous compounds, the SFE extract was not directly analysed on GC. Instead, the product was frozen to –196°C by liquid nitrogen, evacuated and distilled at 60°C into a condenser cooled in liquid nitrogen. The clear condensate was analysed by GC. No significant amount of any terpene could be detected in this distillate by GC. However, TLC of the residue still showed the presence of sesquiterpenoids. Reduced amounts of monoterpenoids in the SFE product may be due to a variety of reasons including reduced solubility and dilution by high molecular weight resin. Also, low volatiles might escape during pressure reduction. SFE might have to be performed at lower temperatures and pressures with trapping of volatiles, if the extract is to retain the characteristic aroma. Further studies are required under varying conditions of extraction for this purpose.

Lantana camara

The plants grow abundantly in North India and leaves were harvested in Delhi during Jan.-Feb. 1996. They were shade dried and extracted. Conditions and yields for liquid CO_2 extraction are given in Table 3. The TLC results showed that pinene and β-caryophylene are present in both hydrodistillate

Table 3 — Liquid CO_2 extraction condition and yield of *Lantana camara*

Sl. No.	Extraction method	Harvest date	Leaf weight g	CO_2 used g	Pressure bar	Temp °C	Time h	Siphon time, min	Yield %
1	SLE	Feb'96	16.3	179	56	19	01.25	5	0.33
2	SLE	Feb'96	16.3	180	55	18	17.30	7	1.84
3	SLE	Feb'96	13.9	178	55	18	04.50	7	1.14

SLE : Subcritical liquid extract

and SLE extract. The GC and GC-MS analysis data are given in Table 4.

The liquid CO_2 extract at 1.25 h was orange with colour deepening to red as the number of extraction cycles increased from 14 to 137. The yield of oil also

Table 4 — Components of *Lantana camara* oil

Sl. No	Component	Hydrodistillate			
		GC-MS		GC	
		RT	Rel-%	RT	Rel-%
1.	L-Phellandrene	8.63	0.46	8.65	1.91
2.	Camphene	9.16	0.45	—	—
3.	α-pinene	9.34	0.43	9.40	2.49
4.	β-pinene	9.65	0.43	9.56	0.48
5.	β-phellandrene	10.62	0.43	—	—
6.	Unidentified	12.71	0.39	—	—
7.	Unidentified	15.90	0.70	—	—
8.	Unidentified	16.08	0.96	—	—
9.	γ-Terpinene	16.74	0.69	16.71	1.10
10.	β-elemene	16.92	3.18	16.86	3.56
11.	Unidentified	17.32	0.53	—	—
12.	β-Caryophyllene*	17.50	27.40	17.50	27.10
13.	Gurjunene	—	—	17.59	1.56
14.	α-Caryophyllene	18.03	13.62	18.02	13.50
15.	Unidentified	—	—	18.14	1.55
16.	α-Copaene	18.21	1.80	18.19	1.91
17.	ε-Murrolene	18.38	3.32	18.38	9.60
18.	γ-Cadinene	18.56	4.76	18.50	4.28
19.	Selinene	—	—	18.60	2.92
20.	α-Cubebene	18.83	1.34	18.81	2.43
21.	β-Farnesene	19.14	5.44	19.07	4.07
22.	D-citronellol	—	—	19.20	0.79
23.	Citral	—	—	19.29	0.41
24.	Geraniol	19.58	0.92	19.51	0.42
25.	Cadinol	19.76	3.11	19.72	0.66
26.	Geranyl acetate	19.89	6.00	19.80	1.86
27.	Unidentified	—	—	19.90	0.63
28.	Bornylacetate	20.07	0.45	19.95	1.94
29.	Unidentified	0.20	1.61	20.24	0.69
30.	Nerol acetate	—	—	20.31	1.02
31.	Unidentified	20.51	5.70	20.55	1.02
32.	Citronellol acetate	20.73	0.38	—	—

*Values for SLE GC : RT =17.50; Rel % =16.0
RT : Retention time

Table 5 — Liquid CO_2 extraction conditions and yields from *Ocimum sanctum*

Sl. No.	Extraction method	Harvest date	Leaf weight g	CO_2 used g	Pressure bar	Temp °C	Time h	Yield %
1.	SLE	Nov'95 green	20 (shade dried crushed)	182	51	15	2.0	0.2%
2.	SLE	Feb'96 green	8	178	58	20	6.5	1.2%

increased from 0.33% to 1.84%. The reported yields by hydrodistillation are in the range 0.23 -0.32%(ref. 40). Hydrodistillation in our laboratory over 8 h yielded 0.2% oil.

Oil Composition

β-Caryophyllene was identified as the major component and together with α-caryophyllene, amounted to 40.6% of the oil. Dutta[40] reported caryophyllene as the major component with 40.8% in Delhi oil and 56.5% in Allahabad oil. Other significant compounds were: L-α-phellendrene, 2%; geraniol (including its acetate), 3%; α- and β-pinene, 2.9%; γ-terpinene, 1.1%; cadinene, 4.28%; elemene, 3.56%; gurjunene, 1.56%; α- copaene, 1.91%; ε-murrolene, 9.6% and farnesene, 4.0%.

Saleh[41] had studied the composition of essential oil of *L. camara* from 5 different varieties, viz. *L. aculeata, L. flava, L. hybrida, L. mistra* and *L. nivea*, obtained from Egypt. Analysis showed the citral followed by caryophyllene and phellandrene as the major compounds, although their percentage varied from variety to variety. These differences were attributed to ecological factors. An interesting observation of the present study is that the components in *L. camara* oil are very similar to that found in *Murraya koenigii* oil (Table 2).

Ocimum sanctum

Ocimum sanctum with green leaves was harvested in Delhi in the months of Nov. '95 and Feb.'96. The condition of extraction and yields are summarized in Table 5. The TLC analysis data showed the presence of eugenol and β-caryophyllene in SLE extract. GC and GC-MS data are given in Table 6.

By GC-MS, thirty peaks could be identified in the liquid CO_2 extract. The major components were : eugenol (43%), methyl eugenol (6.3%) and caryo-

Table 6 — Components of *Ocimum sanctum* oil

Sl. No	Component	SLE GC/MS	
		RT	Rel %
1.	Unidentified	15.03	0.29
2.	Methyl eugenol	16.27	6.32
3.	Eugenol	16.80	43.10
4.	Unidentified	16.92	1.27
5.	Unidentified	17.10	0.56
6.	Unidentified	17.33	2.90
7.	β-Caryophyllene	17.58	12.40
8.	Unidentified	17.89	0.18
9.	α-Caryophyllene	18.09	0.97
10.	ε-Murrolene	18.45	0.65
11.	Cadinene	18.57	8.60
12.	Selinene	18.67	0.36
13.	α-Cubebene	18.87	0.71
14.	β-Farnesene	19.09	0.26
15.	Bornyl acetate	20.03	2.06
16.	Unidentified	20.14	0.54
17.	Unidentified	20.58	1.18
18.	Citronellol acetate	20.70	1.11
19.	Unidentified	20.81	1.98
20.	Unidentified	21.10	1.69
21.	Unidentified	21.50	0.73
22.	Unidentified	21.99	0.95
23.	Unidentified	22.22	0.39
24.	Unidentified	22.75	0.58
25.	Unidentified	24.11	0.62
26.	Unidentified	24.38	0.55
27.	Unidentified	25.01	2.74
28.	Unidentified	25.58	13.13
29.	Unidentified	28.48	0.71
30.	Unidentified	28.63	0.53

phyllene (12.4%). Dey and Choudhuri[16] also reported that in the leaf as well as the stem, the components present were eugenol (57%), methyl eugenol (6%) and caryophyllene (22.5%). The inflorescence and stem also contain these components. Generally these three components together constitute about 85% of the essential oil. In the rest of 15%, seven unidentified components were reported. In the present study, a large number of additional components have been found. Of these, cadinene forms 8.6% and α-caryophyllene about 1%. A number of acetates of terpenes were seen by the Rf values in TLC. For unequivocal identification of all the components further experimentation is needed.

In the CO_2 extract of *O. basilicum* also, eugenol (22.5-23.7%) and methyl eugenol (30.1-37.8%) were reported as the major components[29]. But the presence of caryophyllene was not reported. Besides small amounts of other mono and sesquiterpenes hydrocarbons and acetates reported were : nerol acetate, geraniol acetate and bornyl acetates. All these components have been found in the present study also in less than 1% concentration. The major components reported in French Basil are : linalool, methyl chavicol and eugenol. Other papers which have reported the composition of oil, of other *Ocimum* species include besides major components, methyl cinnamate, dihydrotagetone and eucylaptol. In the case of Greco-basil variety of *O. basilicum*[42], β- caryophyllene has been noted as the major component. Evidently, the composition of *Ocimum* extract vary widely but certain components such as eugenol, methyl eugenol and linalool seem to be most common.

Tagetes patula

In India five species of *Tagetes* are known. In the present study, flowers and roots of *T.patula* were collected from North India. The yield of the extract under different conditions with different sample lots are given in Table 7. TLC data showed that limonene, ocimene and β-caryophyllene were present in SLE and SFE of flowers but not in SFE of roots. In Table 8 and Table 9, the Retention Time (RT) of GC peaks and the identification of the components in the extracts by SLE and SFE, respectively are shown. As is evident from Table 8, the GC peak position of two different extracts of flowers by SLE are comparable

Table 7 — Liquid CO_2 extraction of *Tagetes* flowers and roots

Sl. No.	Extraction method	Weight of material g	CO_2 used g	Pressure bar	Temp °C	Duration of extraction h	Siphon time min	Yield %
1.	SLE	16.1 (crushed) flower	178	57	19-20	7.30	6.0	1.30
2.	SLE	15.6 (not crushed) flowers	182	56	19	6.50	5.7	0.32
3.	SLE	16.2 (not crushed flower)	182	57	20	—	7.0	0.73
4.	SLE	11.7	180	55	18-19	13.50	7.5	4.00
5.	SFE	18.1 (flowers)	—	200	40	0.50	—	0.26
6.	SFE	130 (crushed flowers)	4000	300	40	1	—	1.2
7.	SFE	51 (roots)	—	270	40	0.25	—	0.18
8.	SFE	51 (roots)	—	270	40	0.25	—	0.10

Harvest time for all sample was Feb'96.

Table 8 — Components of *Tagetes* flower oil obtained from liquid CO_2 extraction

Peak No.	Component	SLE I G C		SLE II G C	
		RT	Rel%	RT	Rel%
1.	β-Caryophyllene	17.51	18.70	17.50	17.10
2.	α-Copaene	18.24	0.60	18.23	1.25
3.	Unidentified	18.39	3.16	18.37	3.64
4.	Geranyl acetale	19.90	1.10	—	—
5.	Bornyl acetate	19.97	1.48	19.95	2.00
6.	Unidentified	22.84	21.73	22.82	19.98
7.	Unidentified	22.99	1.79	22.97	3.18
8.	Unidentified	24.12	1.91	—	—
9.	Unidentified	24.77	1.86	—	—
10.	Unidentified	25.47	21.00	25.45	18.20
11.	Unidentified	26.67	1.03	26.65	1.07
12.	Unidentified	28.09	3.14	28.06	2.67
13.	Unidentified	29.16	5.03	29.14	4.46
14.	Unidentified	31.09	1.17	—	—
15.	Unidentified	—	—	32.98	13.31
16.	Unidentified	34.31	4.59	34.28	3.66
17.	Unidentified	34.92	10.09	34.86	9.51
18.	Unidentified	38.40	0.58	—	—

Table 9 — Components of *Tagetes* oil by supercritical CO_2 extraction

S.No.	Component	*Tagetes* Flowers 200 bar dissolved in THF GC		*Tagetes* Flowers 300 bar dissolved in dichromethane GC	*Tagetes* Roots 200 bar in THF GC	
		RT	Rel %	RT	RT	Rel %
1.	Limonene	10.45	16.5	—	—	—
2.	Ocimene	10.50	70.1	—	—	—
3.	Unidentified	—	—	—	16.76	11.2
4.	β-Caryophyllene	17.55	5.1	—	—	—
5.	Unidentified	—	—	—	17.81	17.6
6.	Unidentified	18.54	8.3	18.54	18.49	48.7
7.	Unidentified	—	—	—	22.190	22.3

and reproducible. β-Caryophyllene was identified as one of the major components. Peak corresponding to low volatile mono terpenoids could not be isolated in the SLE. However, TLC showed the presence of limonene and ocimenes.

It is seen in the Table 8 that peak number 6 and 10 are two other major components which are unidentified. From their position it may be concluded that they are not simple terpenoids but derivative products. In SFE of *Tagetes* flowers at 200 bar, the lower terpenoids identified are limonene and ocimene besides β-caryophyllene and a compound at a peak at RT 18.54. SFE of flowers at 300 bar showed only one peak at RT 18.54. SFE of roots of *Tagetes* at 200 bar showed a major peak at RT 18.49 and three peaks at RT 16.76, 17.81 and 22.19, respectively.

The yield of extract for any given duration is more with fluid CO_2 as compared to that by hydrodistillation. However, fluid CO_2, especially under supercritical and high pressure conditions, extracts pigments and resins. The low volatile terpenoids, particular monoterpenes are partially or totally lost in super critical CO_2 extraction possibly during the pressure release time. If these are the desired products steam distillation or liquid CO_2 soxhlet extraction at low temperatures is more suitable. In depth studies are needed with individual components and their mixtures as standards for optimizing the extraction conditions.

Acknowledgements

The financial support to one of the authors (PV) by DAAD (German Academic Exchange) for working at the University of Siegen and the project support by the Department of Science and Technology, New Delhi are gratefully acknowledged. Research Associateship to one of the authors (MT) from CSIR, New Delhi, is also gratefully acknowledged.

References

1 Matsumara F, *Toxicology of Insecticides* (Plenum Press, New York) 1975.

2 Joan Comsock M (Series Editor), *Biologically Active Natural Products, ACS Symposium Series* (1988).

3 Gommers F J, *Meded. Landbouwhogesch Wageningen*, **73-17** (1973) 71; *Chem Abstr*, **81** (1974) 59251 h.

4 Takahashi S, *Pertanika*, **11**(2)(1988) 249-53.

5 Mansour F, Ravid V & Putievsky E, *Phytoparasitica*, **14**(2) (1986) 137-42.

6 Duke S O, Paul R N & Lee S M, *Terpenoids from the Genus Artemesia as Potential Pesticides*, in *Biologically Active Natural Products* (Series Editor : M Joan Comsock) 1988, p 318-334.

7 Elakaivich S D, *Terpenoids as Model for New Agrochemicals*, in *Biologically Active Natural Products* (Series Editor : M Joan Comsock) 1988, p 250 - 261.

8 Bhat S V, *Life Chem Rep*, **12**(2) (1994) 137-80.

9 Sharma R N, *The Utilisation of essential oils and some common allelochemical constituents for non-insecticidal pest management strategies*, in *Proceedings of Symposium Newer Trends Essential Oils Flavours*, edited by K L Dhar, R K Thappa and S G Agarwal (Tata McGraw Hill, New Delhi, India) 1993.

10 Okamura K, Iwakami S & Matsunaga T, *Toyama-ken Yakuji Kenkyusho Nenpo*, **20** (1993) 95-101 .

11 William F & Valerie P J, *Hydrobiologia*, **116-17** (1984) 135- 40.

12 Villarreal M L, Alvarez L, Alonso D, Navarro V, Garcia P & Delgade G, *J Ethnopharmacol*, **42**(1) (1994) 25-9.

13 Regnault-Roger C, Hamraoui A, Holeman M, Theron E & Pinel R, *J Chem Ecol*, **19**(6) (1993) 1233-44.

14 Coats R J, Karr L L & Drewes C D, *ACS Symp Ser*, (1991) 305- 16.

15 Suri R K & Thind T S, *Indian Drugs Pharm Ind*, **13**(6) (1978) 25-8.

16 Dey B B & Choudhuri M A, *Indian Perfumer*, **28**(2) (1984) 82- 87.

17 Deshpande R S & Tipnis H P, *Pesticides*, **11**(5) (1997) 11-12.

18 Hassanali A, Leande W, Ole-Sitayo N, Morcka L, Nokoe S & Chapya A, *Discovery Innovations*, **2**(2) (1990) 91-5.

19 Maruzzella J C, Scrandis D, Scrandis J B & Grabon G, *Plants Diseases Reptr*, **44** (1960) 789-92.

20 Jain P C & Agrawal S C, *Nippon Kizgakkai Kaiko*, **19**(2) (1978) 197- 200.

21 Ohbayashi N, *Kagaku To Seibutsu*, **15**(5) (1977) 297-9.

22 Hethelyi E, Danos B, Tetenyi P & Koczka I, *Herba Hung*, **26**(1) (1987) 49-61.

23 Wels C, Bertach W & Perich M, *Chromatographia*, **34**(5-8) (1993) 241-8.

24 Wealth of India, Raw Materials, Vol 6 (Council of Scientific and Industrial Research, New Delhi), 1962, p 481.

25 Nigam S S & Purohit M, *Perf Essen Oil Rec*, **52** (1961) 643.

26 Prakash V & Natarajan C P, *J Fd Sci Technol*, **11** (1974) 284- 6.

27 Macleod A J & Pieris N M, *Phytochem*, **21**(7) (1982) 1653-57.

28 Gujral G S & Vasudevan P, *J Sci Ind Res*, **42**(5) (1983) 281-6.

29 Tateo F & Verderio E, *J Essent Oil Res*, 2 (March/April, 1989) 97.

30 Wealth of India, Raw Material, Vol 10 (Council of Scientific and Industrial Research, New Delhi) 1962, p 109-112.

31 Hethelyi E, Danos B, Tetenyi P & Juhasz G, *Herba Hung*, **26**(2- 3) (1987) 145-58.

32 Tygadio J A, Maestri D M & Ariza E L, *J Essent Oil Res*, **5**(1) (1993) 85-6.

33 Wells C, Bertsch W & Perich M, *Chromatographia*, **34**(5-8) (1992) 241-8.

34 Wells C, Bertsch W & Perich M, *Chromatographia*, **35**(3-4) (1993) 209.

35 Vasudevan P, Kashyap S & Sharma S, *Bioresource Technology*, (Communicated) (1997).

36 Naik SN, Lentz H & Maheswari RC, *Fluid Phase Equilibria*, **49** (1989) 115-126.

37 Ashok Kumar, *Studies on Liquid and Supercritical Carbon Dioxide Extraction of Indian Spices*, Ph D Thesis, Indian Institute of Technology, Delhi (1996).

38 Wagner H, Bladt S & Zgainski E M, *Plant Durg Analysis* (Springer-Verlag, Berlin) 1983.

39 Millar J M & Kirchner J G, *Anal Chem*, **25** (1953) 405.

40 Dutta S, *Indian Perfumer*, **4** (Pt1) (1960) 15-19.

41 Saleh M, *Planta Med*, **25**(4) (1974) 373-5.

42 Mariani M, Ducci L, Scotti A & Gravina A, *Riv Ital EPPOS*, (1991) 125-37.

Journal of Scientific & Industrial Research
Vol. 56, November 1997, pp 673 - 679

Adsorption of Pb(II) on Photofilm Waste From Aqueous Solution and Wastewater

K Selvaraj* and V Chandra Mohan

Department of Chemistry, P.S.G. College of Arts & Science, Coimbatore - 641 014, India.

Received: 27 August 1997; accepted: 08 September 1997

Photofilm industrial waste sludge has been studied as a sorbent for removal of Pb(II) from aqueous solutions. Effects of contact time, initial concentration of Pb(II), adsorption dosage, particle size and pH have been studied. The adsorption follows first order kinetics. The percent adsorption increased from 24 to 82% with increase in pH from 3.5 to 6.0. The adsorption isotherms of Pb(II) were found to follow the Langmuir adsorption model. Specific ion adsorption via chelation followed by ion- exchange reaction appears to be the principal mechanism involved in the process. Desorption studies showed that 72% of Pb(II) can be desorbed from the adsorbent at pH 3.0. The efficiency of the adsorbent to remove Pb(II) was found to be 99% for the wastewater obtained from radiator industry.

Introduction

Adsorption of Pb(II) ions has been studied by number of researchers using commercial carbon and activated carbons[1-4]. High capital and regeneration cost of activated carbon has resulted in an increasing search of low cost adsorbents. Various low cost adsorbents reported for the removal of lead are barley straw[5], human hair[6], fertilizer waste slurry[7], waste tyre rubber[8], clays and oxide gel[9,10]. In recent years, considerable attention has been devoted to the study of use of industrial wastes as adsorbents. Flyash[11] obtained from thermal power plant and Fe(III)/Cr(III) hydroxide[12], a waste obtained from petrochemical industry were successfully used for metal removal. In the present investigation studies on use of the photofilm industrial waste sludge as a low cost adsorbent for removing lead from aqueous solutions and wastewater and its adsorption characteristics have been reported.

Experimental

Materials

The adsorbent photofilm waste was collected from Hindustan Photofilm Industry (HPF, Udagamandalam, Tamil Nadu, India). It was ground, washed with dilute sulphuric acid to remove acid soluble impurities, soaked in 2% sodium bicarbonate solution till effervescence ceased and allowed to stand overnight in contact with it to remove residual acid, if any. The material was washed with distilled water to remove very fine particles, dried at 100°C for 12 h and sieved to different particle size viz. 0.10-20 mm, 0.15-0.25 mm and 0.25-0.50 mm. The

Table 1 — Characteristics of the adsorbent

S. No.	Parameter	Value
1	Apparent desnsity, (g/ml)	0.74
2	pH	6.60
3	pH_{ZPC}	6.30
4	Mechanical moisture content % (w/w)	7.38
5	Iron (as Fe_2O_3), % (w/w)	2.85
6	Celllulose, % (w/w)	8.56
7	Lignin	12.16
8	Aluminium (as Al_2O_3),,% (w/w)	32.62
9	Loss on ignitition, % (w/w)	38.40
10	Surface area ($m^2/2$)	286.00
11	Particle size (mm)	0.100-0.200

*Author for correspondence

characteristics of the adsorbent are shown in Table 1. A stock solution of Pb(II) (1000 mg/l) was prepared in double distilled water acidified with 1 ml of concentrated nitric acid. The natural waste water was collected from radiator manufacturing industry at Coimbatore. All the chemicals used were of AR grade. For pH adjustments 0.1N HNO_3 and 0.1 N Na OH solutions were used.

Adsorption Studies

Batch adsorption studies were carried out by agitating 50 ml of Pb(II) solutions at desired concentration and pH with 100 mg of adsorbent for different time intervals. At the end of predetermined time intervals, the sorbate was separated by centrifugation and the supernatant was analysed for the remaining lead concentration using Perkin-Elmer 2380 Atomic Adsorption Spectrophotometer. Studies on the effects of initial Pb(II) concentration, adsorbent dosage and particle size at different agitation times were also carried out.

For pH studies 50 ml of the 10 mg/l Pb(II) solution was adjusted to different initial pH values, agitated with 100 mg of adsorbent for 180 min and remaining Pb(II) in the solution was estimated as before.

Desorption studies were carried out as follows. After adsorption experiment with Pb(II) solution of 10 mg/l and 100 mg of adsorbent, the adsorbent was separated and gently washed with distilled water to remove any unadsorbed Pb(II). Several such adsorbent samples were resuspended in 50 ml of distilled water adjusted to different pH values ranging between 3.0 and 7.0 and agitated for 180 min. Then the desorbed Pb(II) was estimated.

The wastewater obtained from radiator manufacturing industry was diluted ten times. For the study of effect of adsorbent dosage, pH of the sample (50 ml) was adjusted to 5.0 and agitated with different absorbent dosage for 120 min. Then the supernatant was centrifuged and analysed for Pb(II).

All the experiments were done in triplicate and the results were reproducible within ± 5% deviation.

Results and Discussion

Effect of Agitation Time and Initial Pb(II) Concentration

Fig. 1 shows that the percent adsorption of Pb(II) on the adsorbent increased with increase in agitation time and attained equilibrium after 120 min. The per cent removal was found to be 92, 84, 73 and 58% at the initial concentrations of 10, 20, 30 and 40 mg/l of Pb(II) respectively. The equilibrium time was found to be independent of Pb(II) concentration. The time curves in Fig. 1 are single, smooth and continuous, leading to saturation suggesting the possibility of

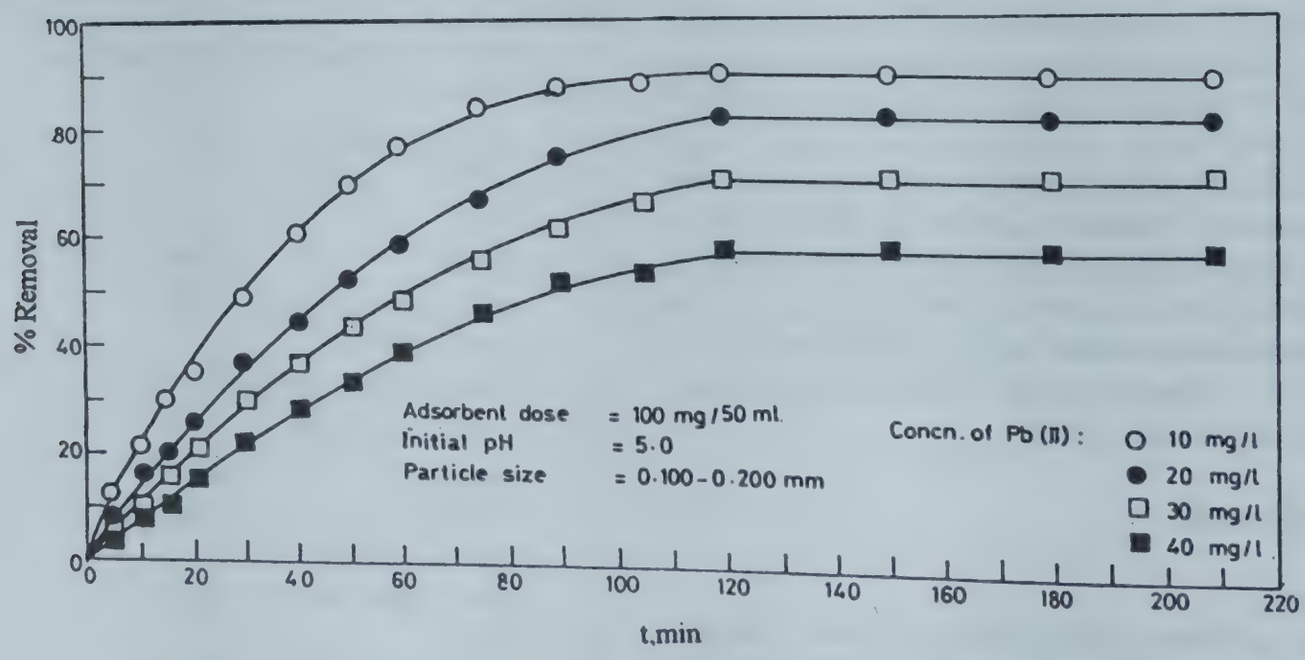


Fig.1 — Effect of agitation time and initial Pb(II) concentration

formation of monolayer coverage of Pb(II) on the surface of the adsorbent.

Effect of Agitation Time and Particle Size

Lead (II) solution of 10 mg/l concentration was agitated with 100 mg of adsorbent of different particle sizes viz., 0.10-0.20 mm, 0.15-0.25 mm and 0.25-0.50 mm for different agitation times. Maximum removal was found to be at 120, 180 and 210 min and the per cent removal was 92,86 and 74% respectively (Fig.2). This shows that decreasing particle size increases the adsorption of Pb(II) on photofilm waste. According to Weber[13] the breaking of larger particle tends to open tiny cracks and channels on the particle surface, providing added surface area which can be employed in the adsorption process. For the large particles, intraparticle diffusion will be the predominant mechanism.

Effect of Adsorbent Dosage

Dosage of adsorbent was varied from 10 mg to 250 mg for 50 ml of 10 mg/l concentration of Pb(II) solution (Fig.3). The result shows that 175 mg/50 ml of the absorbent is sufficient for complete removal

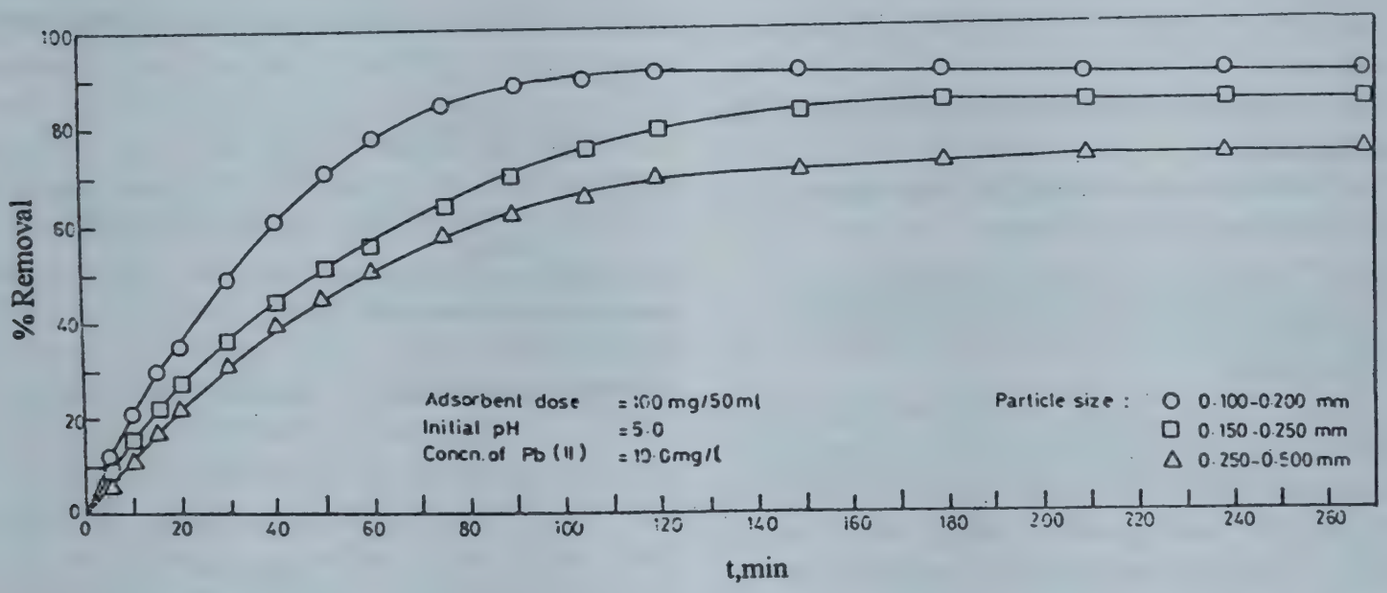


Fig.2 — Effect of particle size on Pb(II) removal

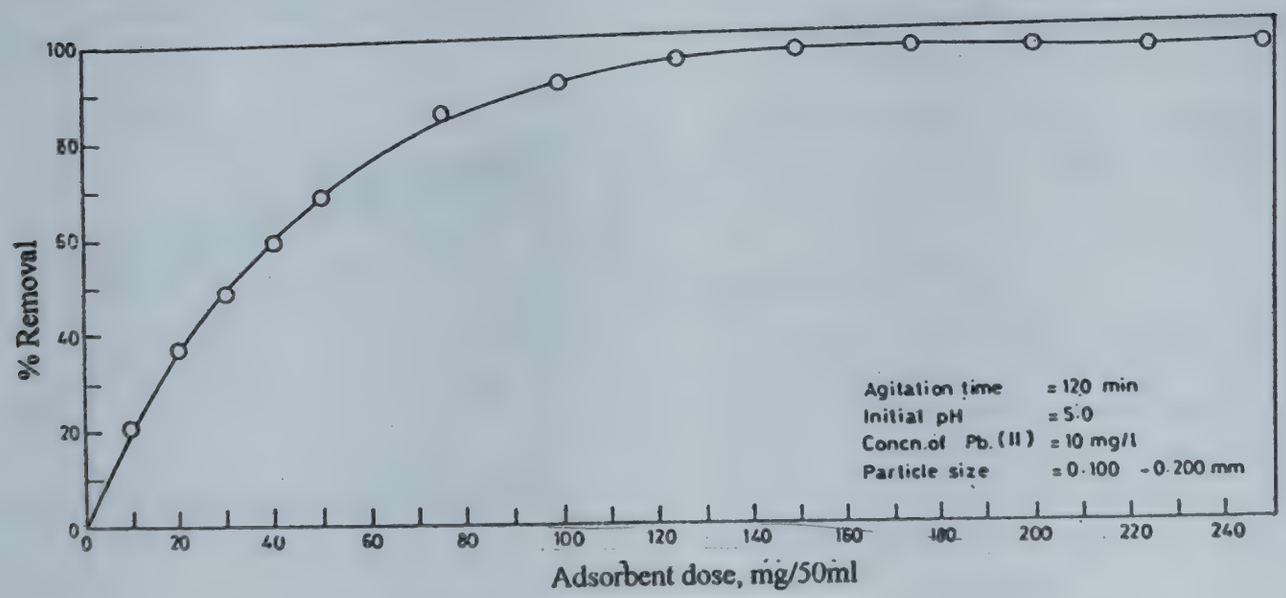


Fig.3 — Effect of adsorbent dosage on Pb(II) removal

of 10 mg/l of Pb(II) at the equilibrium time of 120 min.

Adsorption isotherm

Langmuir equation was applied to study adsorption equilibrium[14]. Langmuir isotherm is based on the assumptions that (i) maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, (ii), that the energy of adsorption is constant, and (iii) that there is no transmigration of adsorbate in the plane of the surface. Langmuir equation is given by

$$\frac{C_e}{q_e} = \frac{1}{Q_o\, b} + \frac{C_e}{Q_o}$$

where

C_e is the concentration of metal ion (mg/l) after equilibrium,

q_e is the amount of metal ion (mg) adsorbed per g of adsorbent after equilibrium

and Q_o & b are Langmuir constants related to adsorption capacity and energy of adsorption respectively.

Plots of C_e/q_e vs C_e (Fig.4) are linear which indicate that the adsorption follows Langmuir isotherm model for Pb(II) Q_o and b were calculated from the slope and intercept of the plot and were found to be 13.33 and 0.59 respectively. Comparison of Q_o values of Pb(II) adsorption on to photofilm waste with that in the literature data indicates that the adsorption capacity of photofilm waste is very much greater than other adsorbents.

The equilibrium parameter[15], R_L is defined as

$$R_L = \frac{1}{1 + b\, C_o}$$

where

C_o is the initial metal ion concentration (mg/l) and b is the Langmuir constant (l/mg)

The R_L values at different concentrations are between 0 and 1.0 indicating favourable adsorption for all the initial concentrations of Pb(II) studied.

Adsorption kinetics

The kinetics of Pb(II) adsorption on photofilm waste follows first order rate expression given by Lagergren[16]

$$\log (q_e - q) = \log q_e - \frac{K_{ad}}{2.303} \times t$$

Table 2 — Effect of Pb(II) concentration on Lagergren rate constant

Adsorbent dose =100 mg/50 ml
Particle size =0.100-0.200 mm
Initial pH =5.0

Concentration of Pb (II) (mg/l)	Rate constant K_{ad} min^{-1}
10	3.68×10^{-2}
20	2.76×10^{-2}
30	2.76×10^{-2}
40	2.30×10^{-2}

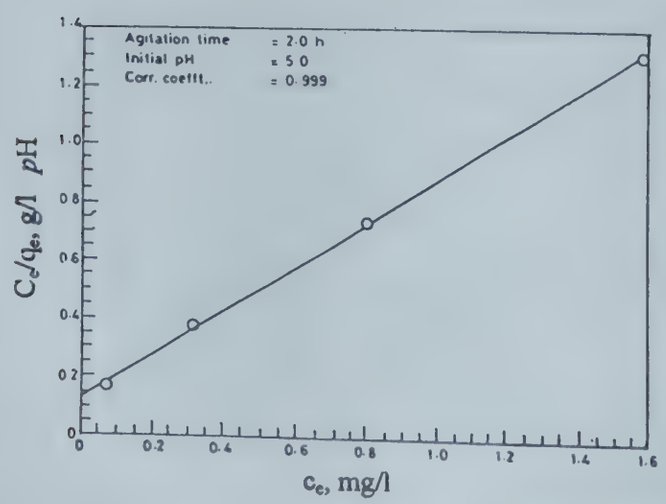


Fig.4 — Langmuir plot for Pb(II) adsorption

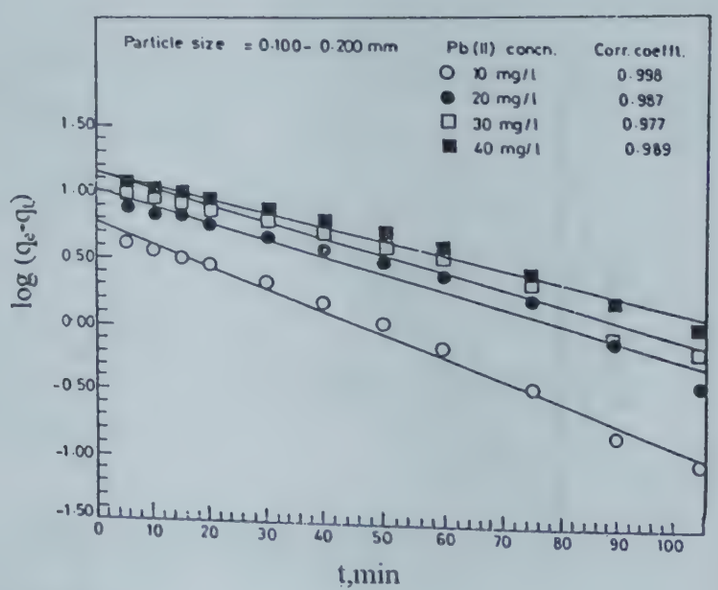


Fig.5 — Effect of metal ion concentration on Lagergren plots for Pb(II) adsorption

where q and q_e are the amounts of Pb(II) adsorbed (mg/g) at time t (min) and at equilibrium time respectively. Linear plots of log q_e vs. t indicate the applicability of the above equation (Fig.5). The K_{ad} values at different initial concentrations are presented in Table 2. The rate constants are higher at lower concentrations and are comparable to those found in literature. The adsorption of Pb(II) by polyacrylamide grafted tin (IV) oxide gel obeyed the Lagergren equation and the value of K_{ad} is 4.15×10^{-2} min^{-1}.

Effect of pH

The influence of pH on the adsorption of Pb(II) by the adsorbent is shown in Fig. 6. For comparison lead hydroxide precipitation by NaOH is also given. Increase of pH increased the per cent removal of Pb(II) both by adsorption and hydroxide precipitation. However, at any pH Pb(II) removal by adsorption is very much greater than by hydroxide precipitation. It was observed that with the increase in pH of the system from 3.5 to 6.0, Pb(II) removal by adsorption increased from 24 to 92%. At higher pH (>6.0) precipitation of Pb(II) takes place[12] and this complicates the removal of Pb(II) adsorption.

The pH_{zpc} (pH at which the adsorbent surface is neutral) of photofilm waste is found to be 6.3. In acidic solutions, the adsorbent surface being positively charged, the adsorption of Pb^{2+} species is not favoured. On the contrary, as the pH increases, the adsorbent surface becomes more and more negative

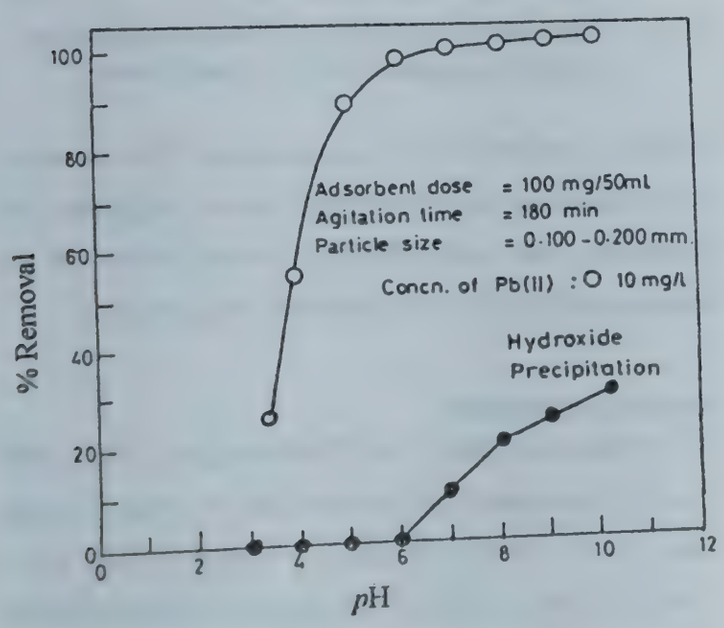
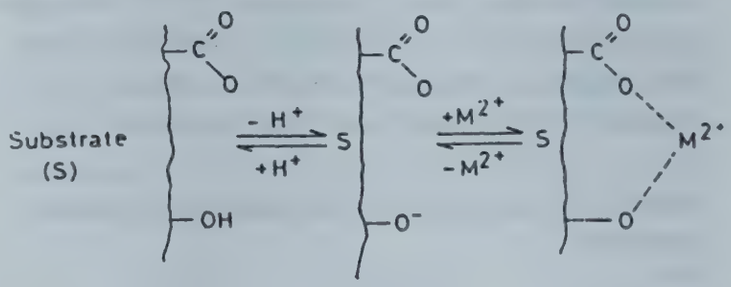

% Removal
pH
Adsorbent dose = 100 mg/50ml
Agitation time = 180 min
Particle size = 0·100 - 0·200 mm
Concn. of Pb(II) : O 10 mg/l
Hydroxide Precipitation

Fig.6 — Effect of pH on Pb(II) removal

charged and the adsorption of Pb^{2+} species is more favourable. Similar results were reported for the adsorption of Pb(II) on hydrous oxide gels of iron[17] and polyacrylamide grafted tin(IV) oxide gel[10]. Appreciable adsorption of Pb(II) also occurs at pH values well below the pH_{zpc} of the adsorbent, though the adsorbent surfaces are more positively charged. Since electrostatic attraction is not possible between positively charged adsorbent surface and positively charged metal ion species, it seems that some non electrostatic forces might be involved in the adsorption[18].

The present adsorbent photofilm waste used contains many components. It consists of oxide of aluminium, iron and organics. The ZPC value of Al_2O_3 is about 5.5. The higher value of ZPC of the present adsorbent (6.3) is due to the presence of multicomponents in the adsorbent.

The existence of organics in the present adsorbent is also responsible for adsorption of metal ions. The organics possess polar functional groups and these may interact with metal ion via complexation, probably chelation, thus removing them from aqueous solution and in addition some degree of ion exchange reaction may occur. The illustration on chelation mechanism is shown in the following figure.



Desorption

Desorption studies help to elucidate the nature of adsorption, recovery of metals from wastewater and recycling of adsorbent. Lowering the pH of the desorbing medium from 7.0 to 3.0 increased the desorption of Pb(II) from 0 to 74% (Fig.7). In the acid medium, protons may compete with Pb(II). Hence it is reasonable to assume that ion exchange mechanism takes place in the adsorption of Pb(II) on photofilm waste.

Test With Industrial Waste Water

The characteristics of radiator manufacturing industry wastewater are shown in Table 3. As it has very high concentration of Pb(II) (401 mg/l) it was diluted ten times and then subjected to treatment. Adsorption of Pb(II) increased from 28 to 99% when the adsorbent dosage was raised from 50 to 550 mg/50 ml (Fig.8). This demonstrates that the photofilm waste can be successfully used for the removal of Pb(II) from radiator industry waste water.

Disposal of Spent Adsorbent

To avoid leaching of Pb(II) into ground water, the lead loaded adsorbent can be stored in impervious barriers[19]. A variety of liner materials include modified betonite, a soil cement, a hydraulic asphalt concrete, chlorinated polyethylene, neothylene, neuprene, butyl rubber and a thermoplastic polyester elastomer.

Conclusions

The present investigation shows that the photofilm waste can be employed as an effective adsorbent for the removal and recovery of Pb(II) from wastewater. At any pH Pb(II) removal by adsorption was very much efficient compared to hydroxide precipitation for Pb(II) concentration of 10 mg/l. Increasing adsorbent dosage and lowering of particle size increased the adsorption. Desorption of Pb(II) from the spent adsorbent was 74% at pH 3.0. Since the adsorbent is disposed as waste by photofilm industry, Pb(II) removal by this adsorbent from industrial wastewaters is expected to be economical. The data may be useful to environmental and sanitary engineers for designing and establishing treatment plant for the removal of Pb(II) from industrial waste water.

Table 3 — Characteristics of radiator manufacturing industry wastewater

S.No	Parameter	Value
1	pH	2.61
2	Turbidity, (NTU)	75.00
3	Total solids, (mg/l)	5220.00
4	Conductivity, (ms/cm)	14.12
5	COD, (mg/l)	260.00
6	Chlorides, (mg/l)	2350.00
7	Sulphate, (mg/l)	96.00
8	Lead, (mg/l)	401.00
9	Sodium, (mg/l)	170.00
10	Calcium (mg/l)	215.00

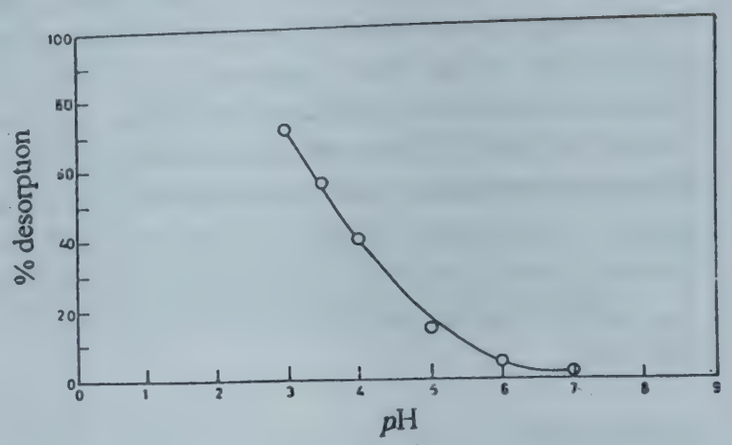


Fig.7 — Effect of pH on desorption of Pb (II)

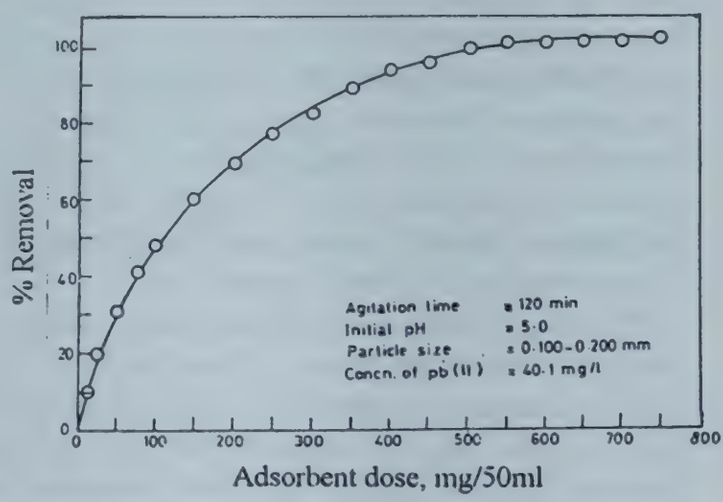


Fig. 8 — Effect of adsorbent dosage on removal of lead from radiator manufacturing industry waste water

Acknowledgement

Authors are grateful to The Manager, R&D, HPF Ltd., Udagamandalam for providing the waste sludge and Dr. B. Sampath Kumar, Principal, and Dr S Pattabhi. Head of the Department of Environmental Science, P.S.G. College of Arts and Science, Coimbatore for providing the laboratory facilities.

References

1 Netzer A & Hughes D E, *Wat Res*, **18** (1984) 927.

2 Corapcioglu M O & Huang C P, *Wat Res*, **21** (1987) 1031.

3 Kuennen R W, Taylor R M, Dyke K V & Groenevelt, K, *J Am Wat Wks Assoc* **84**(1992) 91-101.

4 Brain E Reed & Selvam Arunachalam, *Environ Prog*, **13** (1994) 60-64.

5 Larsen V J & Schierup H, *J Environ. Qual*, **10** (1981) 188-193.

6 Tan T C. Chia, C K & Teo C K, *Wat Res*, **19** (1985) 157-162.

7 Srivastav S K, Tyagi R & Pant N, *Wat Res*, **9** (1989) 1161-1165.

8 Rowley A G, Husband F M & Cunningham A B, *Wat Res*, **18** (1984) 981-984.

9 Yadava K P, Tyagi B S & Singh V N, *J Chem Technol Biotechnol*, **51** (1991) 47-60.

10 Shubha K P and Anirudhan T S, *Indian J Chem Technol*, **3** (1996) 55-57.

11 Viraraghavan T & Rao G A K, *J Environ Sci Health*, **A26** (1991) 721-753.

12 Namasivayam C & Ranganathan K, *Ind Eng Chem Res*, **34** (1995) 869-873.

13 Weber W B & Morris J C, *J Sanitary Eng Div ASCE*, **89** (SA2) (1963) 31.

14 Langmuir I J, *Am Chem Society*, **40** (1918) 1361.

15 Hall K R, Eagleton L C, Acrivos A & Vermeulen T, *Ind Eng Chem Fundam*, **5** (1966) 212-219.

16 Singh A K, Singh D P, Pandey K K & Singh V N, *J Chem Technol Biotechnol*, **42** (1988) 39-49.

17 Kinniburgh D G, Jackson M L & Syers J K, *Soil Sci Soc Am J*, **40** (1978) 796-797.

18 Kinniburgh D G, Syers J K & Jackson M L, *Soil Sci Soc Am Proc*, **39** (1975) 364-370.

19 Haxo H E, Haxo R S & White R M, EPA-68-03-2173 : EPA/600/2- 77-081, *Cincinnati*, OH 1977.

Journal of Scientific & Industrial Research
Vol. 56, November 1997, pp 680 - 685

Synthesis and Characterization of New Composite Ion Exchangers

A Mariamichel* and S Krishnamoorthy+

Department of Chemistry, Regional Engineering College, Tiruchirappalli 620 015, India

Received: 10 July 1997; accepted: 12 August 1997

The charcoal obtained by sulphonating the tannin rich mangroves bark was used to replace the polymeric matrix of phenolformaldehyde sulphonic acid. A few cation exchangers were obtained by varying the substituent content from zero to 100 per cent. The important characteristics of the composites have been determined. Since the composites up to 30 per cent substitution retain the essential properties of pure phenolic cationite and also that the mangroves bark is available freely and in plenty, it is established that the 30 per cent composite is a cheaper cation exchanger.

1 Introduction

Synthesis and characterization of ion exchangers are of interest, because of their large - scale uses in hydrometallurgy, pharmaceutical preparations, sugar industry, pollution control, analytical chemistry, and particularly in water - softening. Since the current commercial exchangers owe their origin to the products of petroleum, there is a phenomenal increase in the cost of the exchangers. Hence, there is an urgent need either to find out new resins which are cheaper than the existing ones or to prepare composite exchangers by partly replacing the polymeric content of the current exchangers considerably while retaining the important characteristics of the parent resin. The composite would be very efficient if the substituent itself could act as an exchanger. Earlier studies show that cheaper composite exchangers could be prepared by partially substituting the macroporous phenolformaldehyde sulphonic acid resin matrix by sulphonated charcoals from coal[1], saw dust[2] spent coffee,[3] cashewnut husk [4], wheat husk[5], turmeric plant[6] (substituted in resorcinolformaldehyde cationic matrices) and spent tea and gum tree bark[7].

*Present Address:
Department of Chemistry, Periyar EVR College,
Tiruchirappalli 620 023, India

+Author for correspondence

The present work deals with the preparation and characterization of composite cation exchangers obtained by incorporating the sulphonated charcoal from the mangroves bark (*Rhizophora apiculata Bl.*) into the macroporous phenolformaldehyde sulphonic acid matrix.

2 Materials and Methods

2.1 Materials and Reagents were the mangroves bark, phenol (BDH sample), formaldehyde solution (37 to 40 per cent, BDH sample) and conc. sulphuric acid (sp gr 1.82)

2.2 Preparation of Phenolformaldehyde Resin

Phenol (10g) and conc. sulphuric acid (23g) were mixed slowly with constant stirring and cooling in ice. The mixture was then heated to 353K for 3 h on a water bath, cooled immediately in ice and kept overnight. It was then polymerized with formaldehyde solution (12.5g) at 353K and the product was further cured for 3 h. The brown coloured chunky solid obtained was ground, washed with distilled water to remove the free acid, dried, sieved and preserved for characterization (sample R).

2.3 Preparation of Composites

The dried mangroves bark (~500g) was carbonized and sulphonated with conc. sulphuric acid (~100g), kept at ambient temperature for 24h and heated to 363K in a hot air oven for 6 h. It was then

cooled, washed free of excess acid and dried (sample SC). A known amount of phenol was sulphonated with conc. sulphuric acid by the above method and calculated quantities of sulphonated charcoal (SC) - were added to it so as to keep the percentage substitution by sulphonated charcoal at 10, 20, 30, 40 and 50, respectively. Each mixture was then polymerized with formaldehyde solution at 353K and the product was further cured for 3 h. It was then ground, washed to remove the free acid, dried, sieved, and preserved for characterization (samples A to E respectively). The experimental and theoretical yields of the composites are reported in Table 1.

2.4 Characterization of Samples

2.4.1 Determination of Physical Properties

The densities of the dry samples (in toluene) and the wet samples (hydrated overnight) were determined by using specific gravity bottles. Swelling measurements were made by allowing the samples to equilibrate in water overnight. The wet weight was taken as *M*w and the corresponding dry weight *M*d was obtained after drying the samples at 343K and then exposing to air. The gravimetric swelling percentage was calculated as given in Eq. (1):

$$\alpha = \frac{Mw - Md}{Md} \times 100 \qquad ...(1)$$

To find out the percentage of attritional breaking, the sample was initially sieved to give particles of 200 μ size. A known quantity (W_1g) of the sample was swollen in water and shaken continuously for 6 h. The wet sample was separated by filtration, dried, sieved on a 200 μ mesh and the amount of the sample which remained on the sieve was weighed (W_2g). From the above weights, the percentage of attritional breaking was calculated to be $W_1 - W_2 / W_1 \times 100$. The values obtained are presented in Table 2. Uniform particle size was maintained by sieving the samples in 200 μ and 300 μ mesh sieves.

2.4.2 Measurement of Column Capacity

A known weight (2g) of the sample was converted into H^+ form by washing with hydrochloric acid (4*M*), followed by distilled water to remove excess

Table 1 — Amounts of reagents used and yields of the composites

Sample	Percentage of sulphonated charcoal (theoretical)	Amounts of reagents used, g					Percentage of sulphonated charcoal (observed)
		Phenol	Formaldehyde	Conc. sulphuric acid	Sulphonated charcoal	Yield g	
R	0	10	12.5	23	0.0000	15.0000	0.00
A	10	10	12.5	23	1.6667	16.0800	10.36
B	20	10	12.5	23	3.7500	18.5500	20.21
C	30	10	12.5	23	6.4286	21.7800	29.52
D	40	10	12.5	23	10.0000	25.0000	40.00
E	50	10	12.5	23	15.0000	30.0000	50.00
SC	100	—	—	—	—	—	—

Table 2 — Densities, gravimetric swelling percentages and attritional breaking of the composites

Sample	Percentage of sulphonated charcoal	Density, gml^{-1}		Gravimetric swelling per cent	Attritional breaking per cent
		Wet	Dry		
R	0	1.3000	1.3550	60.00	8.10
A	10	1.4164	1.4450	50.00	10.20
B	20	1.4164	1.2194	45.50	13.80
C	30	1.4174	1.1820	43.00	15.00
D	40	1.4620	1.2694	40.00	20.20
E	50	1.4368	1.2235	36.00	24.40
SC	100	1.3235	1.2246	30.50	25.30

of H^+ ions. Test column was prepared by using a graduated burette with glass-wool plugs and the slurry of the treated sample. Na^+/ Mg^{2+}/ Zn^{2+}/ Cu^{2+}/ Ca^{2+} solution (40 ml, 0.1M) was added in different portions. The flow of the effluent was adjusted between 1 to 2 ml min^{-1}. The sample exchanged its H^+ ion for Na^+ / Mg^{2+} / Zn^{2+} / Cu^{2+} / Ca^{2+} ion in the solution. The total amount of the cation exchanged was found using standard titration techniques[8]. From the total amount of the cation exchanged, column capacity was calculated and the values (in $mmolg^{-1}$) are presented in Table 3 and Fig.1

2.4.3 Measurement of Absolute Capacity

The sample was taken in H^+ form and its absolute capacity for the exchange of Na^+ ion was determined by pH titration technique[9]. The absolute capacity of the sample with respect to Mg^{2+} / Zn^{2+} / Cu^{2+} / Ca^{2+} ion was determined by adopting Kunin's[10] method. A known weight of the sample was converted into H^+ form with hydrochloric acid (4*M*). Then it was rinsed for removal of excess acid and drained. A portion of the wet sample was dried to find out the percentage of dry weight content. Another weighed portion of the wet sample was introduced into a dry 250ml erlenmeyer flask. To the sample in the flask, standard solution of Mg^{2+}/ Zn^{2+}/ Cu^{2+}/ Ca^{2+} (200 ml, 0.01*M*) was added. The sample in the stoppered flask was kept for 24 h for establishing equilibrium. The sample exchanged its H^+ ion for the said divalent ion. The total H^+ ion exchanged was calculated from the pH change before and after equilibration. The absolute capacity of the sample is finally expressed in m mol g^{-1} dry sample (Table 4). Some absolute capacity measurements were also made with NaOH at pH ~ 13.

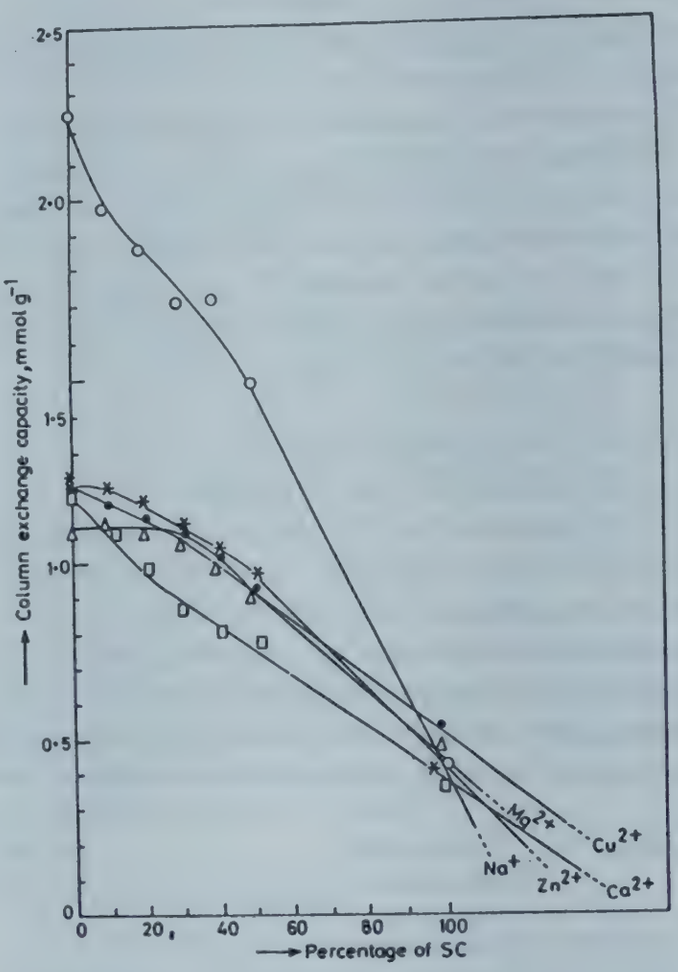


Fig. 1 — Column capacity ;of mangroves bark charcoal composites (Na^+, Mg^{2+}, Zn^{2+}, Cu^{2+}, Ca^{2+} ions, 0.1*M*)

Table 3 — Column capacities of H^+ forms of composites

Sample	Percentage of sulphonated charcoal	Column capacity $mmolg^{-1}$ 0.1*M*				
		Na^+	Mg^{2+}	Zn^{2+}	Cu^{2+}	Ca^{2+}
R	0	2.24	1.23	1.27	1.08	1.18
A	10	1.96	1.14	1.18	1.08	1.01
B	20	1.85	1.11	1.16	1.08	0.96
C	30	1.70	1.07	1.07	1.08	0.86
D	40	1.71	0.96	1.02	0.98	0.78
E	50	1.47	0.92	0.96	0.89	0.74
SC	100	0.43	0.43	0.40	0.49	0.38

Table 4 — Absolute capacity of the samples

Sample	Percentage of sulphonated charcoal	Absolute capacity, $mmolg^{-1}$					
		Na^+ pH 4.5 to 10	Na+ 0.1*M* pH ~ 13	Mg2+ 0.01*M*	Zn2+ 0.01*M*	Cu2+ 0.01*M*	Ca2+ 0.01*M*
R	0	2.250	7.35	1.26	1.26	1.76	2.00
C	30	2.750	7.82	1.26	1.26	1.76	2.00
SC	100	1.300	—	—	—	—	—

Table 5 — Thermal stability of samples

Sample	Percentage of sulphonated charcoal	323 K, g		343 K g		363 K g		383 K g		393 K g	
		Immediate	After 24 h	Immediate	After 24 h	Immediate	After 24 h	Immediate	After 24 h	Immediate	After 24 h
R	0	0.940	1.000	0.930	1.000	0.930	1.000	0.905	1.000	0.700	0.800
C	30	0.950	1.000	0.940	1.000	0.940	1.000	0.940	1.000	0.750	0.850
SC	100	0.995	1.000	0.995	1.000	0.945	1.000	0.990	1.000	0.850	0.900

Table 6 — FT-IR Spectral data of Samples

Sample	Percentage of sulphonated charcoal	S =O str cm^{-1}	SO_2 sym str cm^{-1}	C — S str cm^{-1}	Bonded O — H str cm^{-1}	C — O str O — H def cm^{-1}	CH_2 str cm^{-1}	CH_2 def cm^{-1}	C ⋯ C str cm^{-1}	C — H ⋯ def cm^{-1}
R	0	1032.0	1163.0	581.8	3430.7	1209.1	2924.6 2852.9	1472.5	1594.5	879.1
B	20	1032.0	1163.8	582.5	3412.3	1209.3	2924.8 2850.0	1471.6	1596.6	885.7
SC	100	1036.0	—	584.7	3388.9	1210.5	—	—	1610.6	—

2.4.4 Measurement of Thermal Stability

To measure the thermal stability of the sample, known weights of H^+ forms of the sample were heated separately at 323K, 343K, 363K, 383K and 393K for 1 h in an air oven and immediately weighed. The samples were then exposed to air for 24 h and again weighed. The percentages of the weight loss of the samples are presented in Table 5.

2.4.5 Measurement of Chemical Stability

To measure the chemical stabilities of the samples, the resin and the composites were separately boiled with water and very dilute solution of NaOH for 1 h and the resulting samples were filtered, dried, weighed and their column capacities were found. The results showed no change in the column capacity values from those of the untreated samples. Hence the samples are chemically stable.

2.4.6 Spectral Data

The FT-IR spectra of pure resin, 20 per cent composite and pure charcoal were obtained in KBr pellets by a Bruker 66v spectrophotometer. The frequency data are given in Table 6.

2.4.7 Scanning Electron Micrographs

The Scanning Electron Micrographs (SEMs) of pure resin, 20 per cent composite and pure charcoal were obtained using a JEOL JSM-5300 SEM as shown in Fig. 2 (a - c).

2.4.8 Test for Tannins

The samples except pure resin were separately boiled with hydrochloric acid (2*M*) for 30 min. The red colour produced turned yellowish green on adding neutral ferric chloride solution and again turned red on adding sodium bicarbonate solution[11].

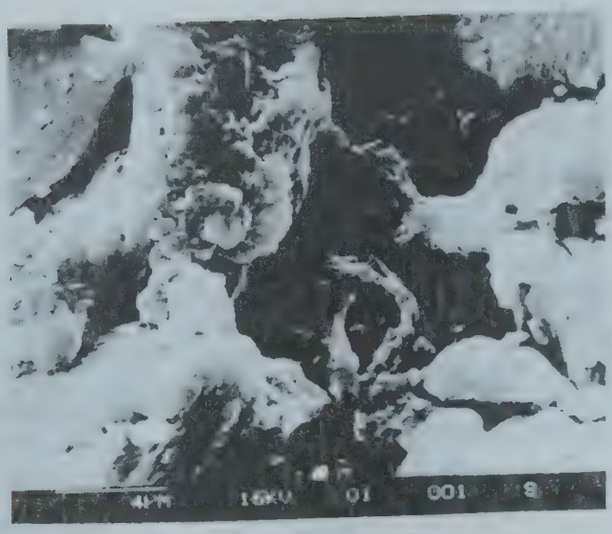


Fig. 2(a) - SEM of SC (x 5000)

Fig. 2(b) - SEM of pure resin (x 10,000)

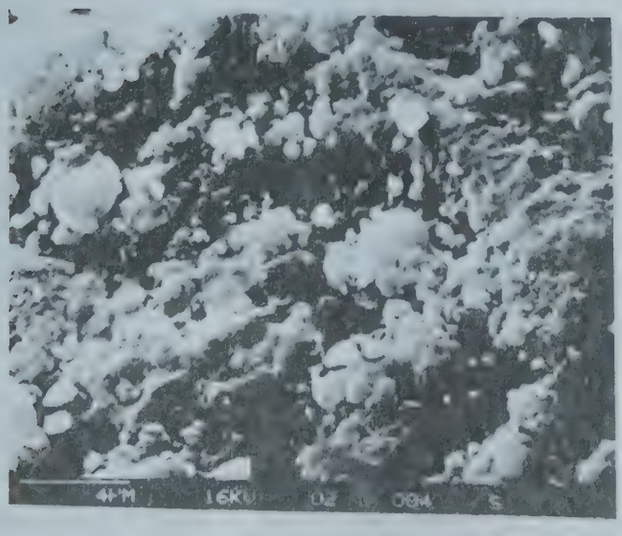


Fig 2(c) - SEM of composite B (x 5000)

2.4.9 The Regeneration Level

The regeneration level for the exhausted ion exchangers, was found by using brine solution (0.01 *M*, 0.05*M*, 0.1*M*, 0.15*M*, 0.2*M* and 0.25*M*, 40ml each) and the results show that 6 mmolg^{-1} of brine solution is the regeneration level for the exhausted ion exchangers.

3 Results and Discussion

The data given in Table I show that the experimental and the theoretical yields of the composites are in good agreement. The data given in Table 2 show that the density of the ion exchangers is quite high, both in dry and wet states. Hence, these composites are suitable for making columns for treating polar and non - polar liquids of high density. Moreover, the wet and the dry density values for each composite are close to each other, thereby showing that they have large pores and hence they are macroporous. The gravimetric swelling percentages decrease from 60 to 30.5 and the values are not very high, because the ion exchangers are macroreticular, having non-gel pores. Based on the attrition data, it is established that the ion exchangers are mechanically stable and the stability is good up to 30 per cent substitution.

From Table 3, it is evident that the pure resin has a column exchange capacity of 2.24 mmolg^{-1} which is comparable to the capacity values of commercial ones such as Amberlite 1R-1, Amberlite IR - 100, Zeo Karb 215, Zeo Karb 315, Wofatit P and Wofatit K. It is also evident that in the composites, the column capacity is greater for Na^+ ion than that for the divalent ions. This may be due to the preferential uptake of the monovalent Na^+ ion by the highly cross-linked and moderately sulphonated phenolformaldehyde system. Among the divalent ions, the column capacity decreases in the following order: $Mg^{2+} \sim Zn^{2+} > Cu^{2+} > Ca^{2+}$, the important factor in concentrated solutions for this trend being ionic size (Mg^{2+} - 0.65Å, Zn^{2+} - 0.74Å, Cu^{2+} - 0.93Å and Ca^{2+} - 0.99Å, ref. 12). Figure 1 shows that the column capacity does not fall appreciably up to the composite (30 per cent). This observation supported by other data like density, swelling, attritional breaking, chemical and thermal stabilities, points to the fact that the composite (30 per cent) is as good as the pure resin itself. Moreover, the mangroves bark is available freely and in plenty. Hence, the pure phenolformaldehydesulphonic acid resin could be substituted

by the mangroves bark charcoal up to 30 per cent which would form a cheap composite ion exchanger.

It can be observed from Tables 3 and 4 that the absolute capacity of the pure resin matches the column capacity with respect to Na^+ ion in 0.1*M* concentration, indicating the attainment of equilibrium rapidly in the column itself. The absolute capacity of the composite is higher than that for the pure resin by about 0.5 mmol g^{-1} with respect to Na^+ion. This may be due to the ionizable - OH groups (at pH 4.5 to 10) present in the charcoal obtained from tannin rich mangroves bark. At pH ~ 13, the composite has higher capacity for Na^+ion from NaOH. This may be due to all the phenolic groups present in the composite in addition to sulphonic acid groups. Among the divalent ions in 0.01 *M* concentration, the absolute capacity increases in the following order: $Mg^{2+} = Zn^{2+} < Cu^{2+} < Ca^{2+}$, the major factor being hydrated ionic radii [13].

Table 5 shows that when the samples are heated up to 383K, initially they lose weight but the lost weights are regained after exposure to air for 24 h. Moreover, at 393K, even after exposure to air, there is a weight loss of 10 to 20 per cent. This observation shows that the ion exchangers are thermally stable only up to 383 K.

An analysis of the data given in Table 6, shows that the samples have strong absorption bands at 1032 — 1036 cm^{-1} (S =O str), strong bands at 1163 — 1163.8 cm^{-1} (SO_2 sym str) and bands at 581 — 585 cm^{-1} (C — S str) thereby confirming the presence of sulphonic acid groups in them. The absorption bands at 2850 – 2925 cm^{-1} (CH_2 str) and at 1471 – 1473 cm^{-1} (CH_2 def) confirm the presence of CH_2 groups in the pure resin and composites. The bands at 1594 – 1611 cm^{-1} (C ⋯ C str) confirms the presence of aromatic rings in the samples. The weak absorption bands at 879 – 886 cm^{-1} in the resin and the composite indicate that some benzene rings are tetra-substituted.

Scanning electron micrographs (SEM) in Fig. 2 (a - c) reveal that the charcoal and pure resin are macroporous, the pore diameter ranging 10^3 to 10^5 Å and also that the charcoals form the reservoir in which the sulphonated phenolformaldehyde resin particles are deposited.

4 Conclusions

Among the composites prepared, the composite containing mangroves bark charcoal up to 30 per cent is found to have high density values, good swelling behaviour, comparable attritional resistance, efficient column and absolute capacities, sufficient thermal stability, and is particularly macroporous and cheap. Hence, it may form a cheaper substitute for the costlier sulphonated phenolformaldehyde resin.

References

1 Sarma NLN, Joseph Mary & Vasudevan Padma, *Res Ind*, **21** (1976) 173 - 178.

2 Vasudevan Padma & Sarma NLN, *J Appl Polym Sci*, **23** (1979) 1443.

3 Mohan Rao GJ & Pillai SC, *J Indian Inst Sci*, **36A** (1954) 70 - 76.

4 Shah HA & Bafna SL, *J Appl Chem, Lond*, **8** (1953) 335.

5 Dheiveegan T & Krishnamoorthy S, *J Indian Chem Soc*, **65** (1988) 731 - 732

6 Kathiresapandian D & Krishnamoorthy S, *Indian J Technol*, **29** (1991) 487 - 488.

7 Mariamichel A & Krishnamoorthy S, *Asian J Chem*, **9** (No. 1) (1997) 136 - 148.

8 Vogel AI, *Text Book of Quantitative Chemical Analysis*, revised by G H Bassett, J Jeffery, J Mendham and RC Denney, *Fifth Edn* (Longman Group Ltd, London) 1989, pp 186 - 192.

9 Helfferich F, *Ion Exchange* (McGraw - Hill Book Co, New York) 1962, pp 5 - 21 and 81 - 83.

10 Kunin R, *Ion Exchange Resins* (John Wiley and Sons, New York) 1958, pp 1 - 54.

11 Harborne *JB, Phytochemical Methods — A Guide to Modern Techniques of Plant Analysis* Second Edn (Chapman and Hall, London) 1984, pp 84 - 90.

12 Pauling L, *J Am Chem Soc*, **49** (1927) 765; *Proc Roy Soc. (London)* **A114** (1927) 181.

13 Wiklander L, *Ann Royal Agri Coll, (Sweden)* **14** (1946) pp 1 - 171.

Journal of Scientific & Industrial Research
Vol. 56, November 1997, pp 686 - 690

Surface Active Properties of N,N-bis (2-Hydroxyethyl) Fatty Amides Derived from Pilu Fat

R P Patel and V M Mannari*

Department of Industrial Chemistry, V P & R P T P Science College, Vallabh Vidyanagar, Gujarat 388 120, India

Received: 25 February 1997; accepted: 01 July 1997

Raw pilu fat (*Salvadora oleoids*) after refining by physical and chemical method was subjected to alkali catalytic aminolysis reaction with diethanolamine to yield N,N-bis (2-hydroxyethyl) fatty amides. These fatty diethanolamides have been characterised by physical, chemical, and IR methods. Various surface active properties of these amides have been studied and compared with those of coconut diethanolamides derived under exactly identical reaction conditions from refined coconut oil.

Introduction

The diverse applications of surface active agents across the industrial spectrum, the demanding requirements of their performance, and the regulatory environmental restrictions have lead to the need for product innovation. In order to produce consumer goods there is a strong move in some sections of the surfactant producers to move away from petrochemical based feed stock. Surfactants made from natural materials other than petroleum are increasingly replacing the petrochemical based products in almost all areas of applications. It is for these reasons that more attention is being given for the products derived from vegetable oils and fats.

Pilu fat (*Salvadora oleoids*) is commercially available in India but it mainly finds low value applications such as in soap making. Despite its very attractive fatty acid composition, its utility in high value applications is mainly limited due to its objectionable colour.

In the present study, raw pilu fat has been refined and characterised by determining various physical and chemical properties. The fatty acid composition of refined pilu fat has been determined by GLC and is presented in Table 1.

*Author for correspondence

The characterisation of refined pilu fat reveals that its fatty acid composition and various physical and chemical characteristics are very close to those of coconut oil (Table 1). Since pilu fat is less expensive

Table 1 — Characteristics of refined oils

Sl No.	Characteristics	Pilu fat	Coconut oil
1	Acid value (mg,KOH/g)	2.0	1.0
2	Saponification value (mg,KOH/g)	253.0	257
3	Iodine value	7.0	8.5
4	Hydroxyl value (mg	KOH/g)	3.0
5	Specific gravity	0.910	0.92
6	Refractive index (@ 30°C)	1.428	1.422
7	Colour (Lovibond Y +5R)	6.0	0.6
8	Fatty acid composition (per cent by wt)		
	(i) Caprylic acid	8.6	6.0
	(ii) Capric acid	5.3	6.0
	(iii)Lauric acid	52.8	44.0
	(iv) Myristic acid	32.0	18.0
	(v) Palmitic acid	1.3	11.0
	(vi) Stearic acid	—	6.0
	(vii) Oleic acid	—	7.0
	(viii) Linoleic acid	—	2.0

than coconut oil, it has been thought to replace coconut oil with pilu fat in synthesising certain group of surfactants and to explore its suitability.

Coconut diethanolamide, derived from coconut oil is a very important surface active agent commercially used in large volumes. It finds applications in liquid and powder detergents, shampoos, textile auxiliaries, as emulsifier, plastic additives, and metal working fluid[1].

Here, fatty diethanolamide from refined pilu fat [N, N - bis(2- hydroxyethyl) fattyamide] (HEPA) has been synthesised and characterised by various physical, chemical, and IR methods.

Various surface active properties of HEPA have been studied and compared with fatty diethanolamide from coconut oil (HECA) prepared from refined coconut oil under identical experimental conditions that were employed in the synthesis of HEPA.

Experimental

Raw pilu fat having yellowish green colour was procured from a local commercial manufacturer and was used for characterisation and synthesis of HEPA after refining[2]. Coconut oil used in the study was a commercial sample and was used without any further purification. Diethanolamine, other chemicals and reagents used were of laboratory reagent grade.

Materials and Methods

Refining of Pilu Fat

Pilu fat (250 g) was taken in a 500 ml 3-neck flask attached with a mechanical stirrer and an inlet for dry nitrogen gas. Fat was heated under stirring to 50°C and concentrated H_2SO_4 (2.5 g) was added, followed by hydrogen peroxide [30 per cent by wt 5.0 g]. It was further heated to 80°C and activated earth (10.0 g) and charcoal (5.0 g) were added and the mixture was stirred for 30 min. The hot mixture was then filtered, washed with hot water to remove residual acid and finally dried over anhydrous sodium sulphate. The refined pilu fat was characterised for various physical and chemical properties[3]. The characteristics and fatty acid composition, as determined by GLC, are reported in Table 1.

Synthesis of HEPA

Fatty diethanolamide from pilu fat was synthesised as reported earlier for linseed oil[4].

Pilu fat (100 g) was heated with diethanolamine (50 g) in a 3- neck flask attached with a mechanical stirrer and an inlet for dry nitrogen gas. The contents were heated to 120°C and zinc oxide (0.02 mole based on wt of pilu fat) was added. It was further heated to 200°C for 25 min. The completion of reaction was confirmed by thin layer chromatogram[5]. HEPA was purified from glycerol and other water soluble impurities by washing the solution of reaction mixture in diethyl ether with 15 per cent aqu. NaCl followed by washing with distilled water. HEPA was then separated from ether solution by distilling off ether in hot water-bath. HECA was synthesized from coconut oil using identical process that was used for HEPA.

Various physical and chemical properties of HEPA and HECA were determined by standard methods[3] and are presented in Table 2. IR spectra of HEPA is presented in Fig.1.

Surface Active Properties

Surface Tension

Surface tension of aqu. solutions of HEPA and HECA having varying concentration were determined by Jager's method. The results are given in Fig.2.

Table 2 — Characteristics of HEPA and HECA

Sl No.	Characteristics	HEPA	HECA
1	Acid value (mg of KOH/g)	2.0	1.0
2	Hydroxyl value (mg of KOH/g)	376	389
3	Iodine value	3.0	6.0
4	Specific gravity	0.98	0.98
5	Colour (Gardner) (Y +5R)	9.0	3.0
6	Nitrogen content (per cent by wt) (By Kjeldhal's method)	4.82	4.42

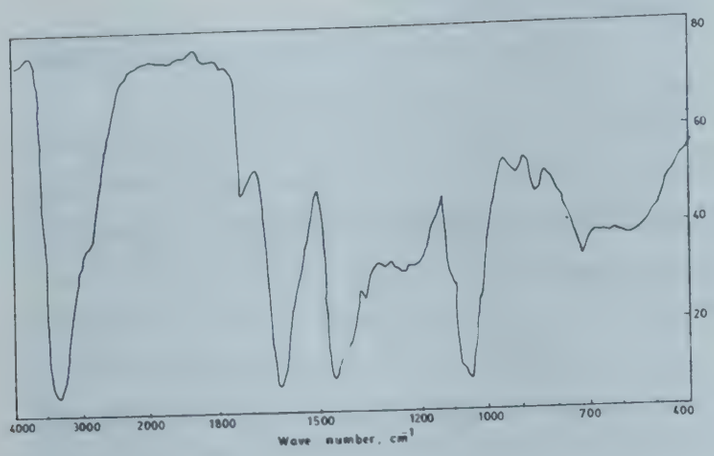


Fig. 1 — IR spectra of HEPA

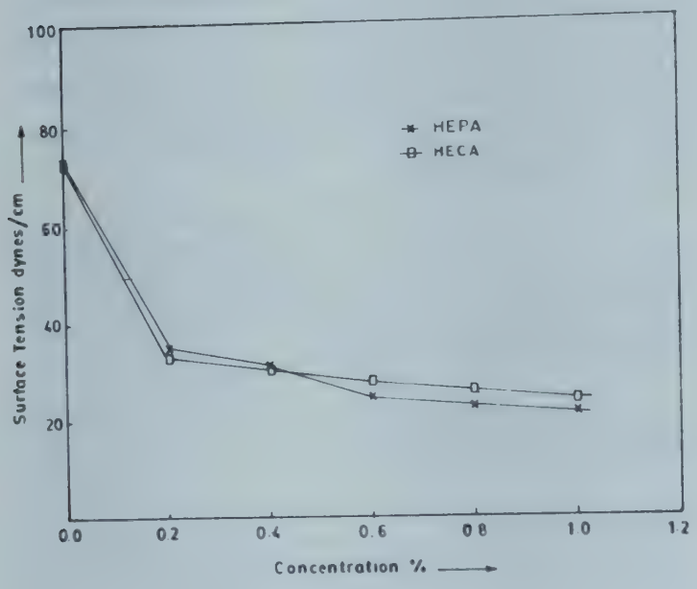


Fig. 2 — Surface tension

Emulsifying Power

Emulsifying power of aqu. solutions of HEPA and HECA having varying concentration were determined by earlier reported method[6]. In a 250 ml stoppered measuring cylinder, 40 ml of sample solution and 40 ml of liquid paraffin were taken. Cylinder was inverted and restored 60-times in 2 min and then kept vertical without disturbing the contents. Time taken for separation of 10 ml of water was noted. The results of emulsifying power of HEPA and HECA are presented in Fig.3.

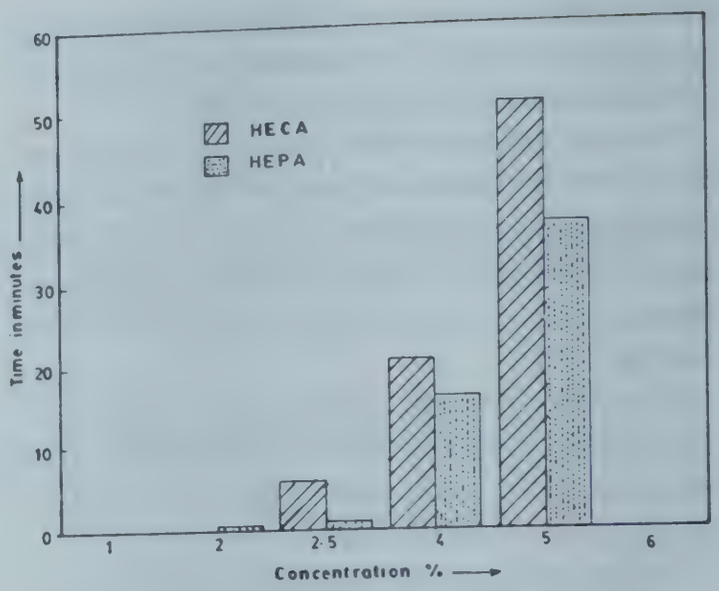


Fig. 3 — Relative emulsifying power

Foaming Power

Foaming power of various solutions of surfactants was evaluated by a known method[7] by determination of foam volume and foam stability of solutions having varying amounts of HEPA and HECA. Twenty-five ml of solution was placed in a 100 ml graduated stoppered cylinder. The cylinder was inverted and restored 60- times in 2 min. The foam heights were measured immediately and after 5 min. Foam stability was calculated using Eq.(1).

$$\text{Per cent foam stability} = \frac{H_i-(H_i-H_r)}{H_i} \times 100, \quad \ldots (1)$$

where H_i=Initial foam height, H_r=Foam height after 5 min.

The results of foaming power are given in Table 3 and results of foam stability are presented in Fig.4.

Relative Dispersity Power

Relative dispersing powers of surfactants were determined by a standard method[8].

In a 250 ml graduated cylinder, 4.0 g of carbon black was taken and 5.0 ml of white oil and sufficient solution of surfactant were added to make total volume of 250 ml. The cylinder was then stoppered and holding it upright it was tilted in the clockwise direction to invert with stopper down and restore back in the same way. This procedure was repeated 10-times and then cylinder was kept stationary without disturbing the content.

Table 3 — Foaming power of HEPA and HECA

Sl No.	Per cent by wt	HEPA			HECA		
	Surfactant	Initial height, cm	Height after 5 min, cm	Per cent foam stability	Initial height, cm	Height after 5 min, cm	Per cent foam stability
1	1.0	0.9	0.45	50	1.2	0.75	62.5
2	2.0	1.0	0.55	55	1.3	0.90	69.2
3	3.0	1.2	0.70	58.3	1.5	1.15	76.7
4	4.0	1.4	0.90	64.2	1.6	1.35	84.0
5	5.0	1.5	1.05	70	1.7	1.60	94.1

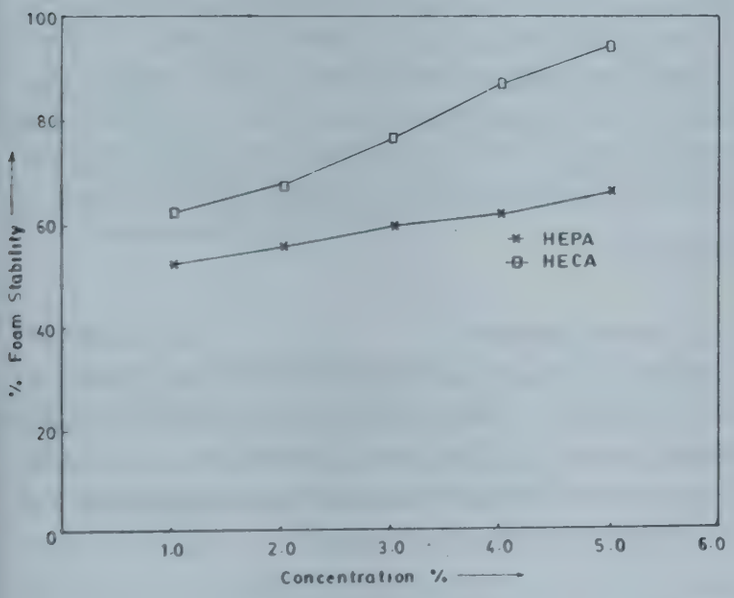


Fig. 4 — Foam stability

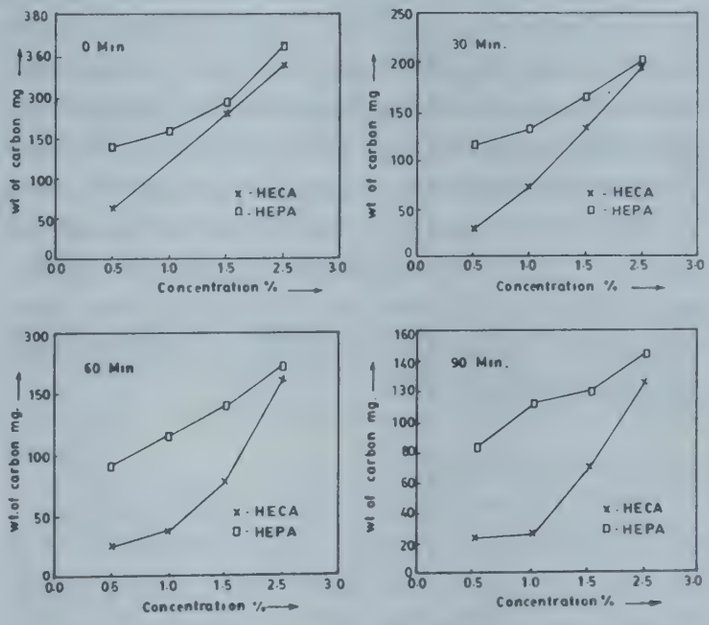


Fig. 5 — Relative dispersing power

5.0 ml of sample from the centre of the cylinder was pippetted out at definite intervals and transferred into a previously weighed petridish. The carbon content of this aliquot was calculated by gravimetric method.

The test for all the solutions having varying surfactant content was performed simultaneously, in duplicate. The results of the test are presented in Fig.5.

Results and Discussion

Synthesis of Fatty Diethanoamides from Refined Pilu Fat

From the known methods for synthesising fatty diethanolamides such as those involving fatty acids or their methyl esters, the one based on aminolysis of oil with diethanolamine has been selected[4]. This single step method is most convenient and economical. Further, it facilitates the removal of by-products (glycerol) along with unreacted materials and catalyst, giving rise to more than 96 per cent pure product.

The IR spectra of HEPA is presented in Fig.1. A strong absorption band at 1050 cm^{-1} is due to C-O stretching of primary alcohol. A band at 1460 cm^{-1} and 1610 cm^{-1} can be attributed to C-H bending and to 3°amide, respectively. A weak band at 1725 cm^{-1} is thought to arise from amide carbonyl group. A broad band at 3350-3400 cm^{-1} confirms the free hydroxyl groups present in the compound. Further, the absence of any strong band at 1740 cm^{-1} indicates replacement of ester carbonyl groups (of oil) by amide groups.

The physical and chemical characteristics of HEPA and HECA are presented in Table 2. The hydroxyl value of HEPA is found to be 376 mg of KOH/g which is consistent with purity of about 96 per cent.

Surface Active Properties

Surface Tension

Figure 2 shows the surface tension of aqu. solution of HEPA and HECA as a function of concentration. From the results, it has been found that HEPA shows surface active properties, surface tension of aqu. solution decreases significantly with increase in concentration of the HEPA up to 0.2 per cent beyond which increase in HEPA concentration has only marginal effect on surface tension of solution. This indicates that the optimum concentration required for the formation of a monolayer of surfactant on the surface is 0.2 per cent. The comparison of results for HEPA and HECA reveals that both the compounds show comparable properties with HEPA thereby showing slightly higher activity.

Relative Emulsifying Power

Figure 3 represents the relative emulsifying power of HEPA and HECA at varying concentrations. From the figure it is clear that relative emulsifying power of both the compounds increases with increase in their concentration and that HECA is far more superior than HEPA in emulsifying property over the entire range of concentrations employed in the study.

Relative Foaming Power

Figure 4 demonstrates relative foaming power of the surfactants in terms of foam stability at varying concentrations. The results reveal that for a given concentration, the foam height and per cent foam stability for HECA are higher than those for HEPA, indicating the relatively higher foaming power of HECA over the range of concentrations studied.

Relative Dispersing Power

Figure 5 (a-d) demonstrate relative dispersion power of HEPA and HECA at 0, 30, 60, and 90 min, respectively. From this figure, it is clear that HEPA has substantially higher dispersing power than HECA over the range of concentrations and time studied.

Concluding Remarks

The study reveals that refined pilu fat can be successfully employed in preparation of fatty diethanolamides for many industrial applications.

The study of HEPA for various surface active properties and its comparison with HECA reveals that HEPA shows certain valuable surface active properties for industrial applications. The comparison of the two reveals that HEPA is inferior in relative emulsifying and foaming properties while it is much superior in relative dispersing power than HECA. Because of low cost of pilu fat, HEPA can partly replace HECA in many applications. HEPA due to its better dispersing power may be useful in Industry.

Acknowledgement

The authors are grateful to Dr H K Patel, Principal, V P & R P T P Science College and Mr K M Patel, Head, Industrial Chemistry Department, for providing necessary facilities for carrying out the study and for their continuous inspiration.

References

1 *Industrial Applications of Surfactants-1*, edited by Karsa (Royal Society of Chemistry) 1990, 132.

2 Bringi N V, *Indian Pat.* 136300 (to Hindustan Lever Ltd), 1972.

3 IS-548 (Part-I), *Indian Standard Methods of Sampling and Test for Oils and Fats* (Indian Standards Institution, New Delhi, 1976.

4 Varghese T M & Krishnan V, *J Colour Soc*, **28** (1990) pp 1-5.

5 Gast L E, Schneider W J & Cowan J C, *J Am Oil Chem Soc*, **43** (1996) 418.

6 Wrigle A W, Smith F D & Stirton A J, *J Am Oil Chem Soc*, **34** (1957) pp 39.

7 Ahmed I & Singh J, *J Am Oil Chem Soc*, **67** (1990) pp 205-206.

8 IS: 5785 (Part-I), *Methods for Performance Tests for Surface Active Agents Part-I, Relative Dispersing Power* (Indian Standards Institution, New Delhi) 1970.

Journal of Scientific & Industrial Research
Vol. 56, November 1997, pp 691 - 695

Studies on Drying of Arvi

U S Shivhare*, K Kaur and A S Bawa

Department of Food Science and Technology, Guru Nanak Dev University, Amritsar 143 005, India

Received: 25 June 1997; accepted: 28 August 1997

Drying of arvi (*Colocasia*) was carried out in a cabinet dryer at 57°C. The treatments prior to drying included blanching of arvi (both cross-sectionally- and longitudinally- cut) in boiling water for 2 min (water-blanching) and water blanching followed by cooling and dipping the samples in 0.5 per cent KMS solution at room temperature for 2 min. The drying rate curves indicated that the drying of arvi takes place in the falling rate period. The Page's model adequately described the drying behaviour of arvi. The overall acceptability was higher for the samples blanched in hot water followed by dipping in KMS solutions; and subsequent drying at 57°C.

Introduction

Drying is the most commonly and widely used method of food preservation. India is one of the few countries in the world having varying climatic conditions from temperate to sub-tropical to tropical, conducive for the growth of various fruits and vegetables. It is the second largest producer of fruits and vegetables in the world with an annual production of about 30 MT fruits and 60 MT vegetables. However, only about one per cent of the total produce is used for further processing. About 20 to 30 per cent of the total production is spoiled, leading to a monitory loss of over Rs 4000 crore due to poor post-harvest management, packaging, handling, and transport systems as well as inadequate cold-storage facilities. Keeping these factors in view, losses can be considerably reduced if the fresh produce is immediately processed at or around the farm by suitable methods of preservation. Drying is one of such technique successfully used in enhancing the shelf-life of food materials. By reducing the moisture content to less than 10 per cent, the opportunity for microbial deterioration is eliminated and the rates of other deteriorative changes are significantly lowered. In addition to preservation, drying results in reduced product mass and volume. Dried vegetable products, however, are not very popular in India and there is an urgent need to conduct basic studies to investigate the effects of various process parameters on the drying rate, total drying time, and quality of the dried product.

Arvi (*Colocasia antiquorum*), a native of the South-East Asia, is an important vegetable of the warm season. The tubers are rich in starch and are utilized in a similar manner as potato, the flesh is mealy and possesses a delicate nutty flavour when cooked. Shelf- life of arvi is about two weeks under refrigerated conditions. Several investigations have been undertaken in the recent past to study the drying behaviour of selected fruits and vegetables[1-10]. Although the vegetable is of good economic value, processing of arvi has not so far received attention of the processors. The present study was therefore undertaken to study the drying behaviour of arvi under selected conditions of pre-treatments and drying air temperature. The quality of the dried arvi was assessed in respect of the dehydration ratio, rehydration ratio, reconstitutability, and overall acceptability based on appearance, texture, and taste.

Materials and Methods

Fresh arvi was purchased from the local market, manually peeled, washed with potable water and placed on sieve to drain out surface water. The peeled arvi was cut into both cross-sectional and longitudinal sections. The cross-sectionally cut samples were

* Author for correspondence

cylindrical in shape being about 2 cm in diam and 0.5 cm thick. Longitudinally cut samples were approximately 5 cm long and 0.3 cm thick. Both cross-sectionally and longitudinally cut pieces were blanched at 100°C for 2 min. Blanching was done by placing the cut pieces in a muslin cloth, followed by dipping in boiling water for 2 min. The blanched samples were cooled by dipping them in cold water. The samples were then spread on a sieve to drain out excess water. The hot water blanched samples will henceforth be referred to as the "water- blanched" samples. Another sample was prepared by blanching at 100°C for 2 min, followed by dipping in 0.5 per cent KMS solution for 2 min at room temperature ("KMS- blanched sample"). The excess water was drained out by placing the samples on a sieve. Fresh cut samples without any pretreatment were considered as the "control". Drying of these samples was carried out at 57 ± 1°C in a cabinet dryer. The cabinet dryer was adjusted to the selected temperature, at least 0.5 h before the start of experiment. The samples of about 1.5 kg initial mass each were uniformly spread on the trays to be subsequently placed in the drying chamber. The observations on the moisture loss were taken at every 0.5 h interval by withdrawing about 5 to 10 g sample for moisture analysis. The samples were turned after 1 h to achieve uniform drying. The drying was continued till the material was dried to approximately 10 per cent moisture content (dry basis). The dried samples were cooled to room temperature and immediately packed in polyethylene bags for further analysis. Moisture content was determined according to the method suggested by Ranganna[11]. The moisture content values, based on the dry matter, were expressed in per cent.

Dehydration ratio, rehydration ratio, and reconstitutability were determined by the methods suggested by Ranganna[11] and Kumar *et al.*[5]. The sensory evaluation of there constituted sample was carried out by a semi-trained panel consisting of seven judges for the overall acceptability based on appearance, texture, and taste using a nine point Hedonic scale[12].

Results and Discussion

Understanding of the drying kinetics and the drying rate of a particulate material is essential to design a dryer for the same. The drying kinetics represents how the drying process is approaching to its equilibriums; whereas the drying rate signifies the rate at which the moisture is being removed from the material. For a particular material, the drying rate depends on the initial moisture content and the condition (temperature, humidity, and flow rate) of the drying air. The drying rate characteristics of a material establish, whether the material is being dried under the constant rate- or falling rate- period, or both. Application of the mathematical models, also called the "drying models" depends on under which period the drying takes place. Since no literature is available on the drying period, the drying rate for arvi was computed using the numerical differentiation technique. The Lagrangian differentiation technique[13] using three data points was used to calculate the drying rate. For equally spaced time intervals, the three-point differentiation formulae are represented, as given in Eqs (1-3).

$$dm_1/dt = [-3m_1 + 4m_2 - m_3] / 200\,\Delta t, \quad ...(1)$$

$$dm_2/dt = [-m_1 + m_3] / 200\,\Delta t, \quad ...(2)$$

$$dm_3/dt = [m_1 - 4m_2 + 3m_3] / 200\,\Delta t \ldots \quad ..(3)$$

where dm_i/dt - drying rate at the ith time, (g moisture)/(g dry matter/h), m_i - moisture content at the ith time, per cent (dry basis), Δt - equally spaced time interval, h.

Equation (2) gives the drying rates at the central points. The drying rate values at the extreme points were computed by Eq. (1) and (3). Equation (1) was used to calculate the rate for the first data point, whereas Eq. (3) was used for the last data point. The time interval was kept at 1 h. The drying rates for untreated (control) arvi are shown in Fig. 1. It indi-

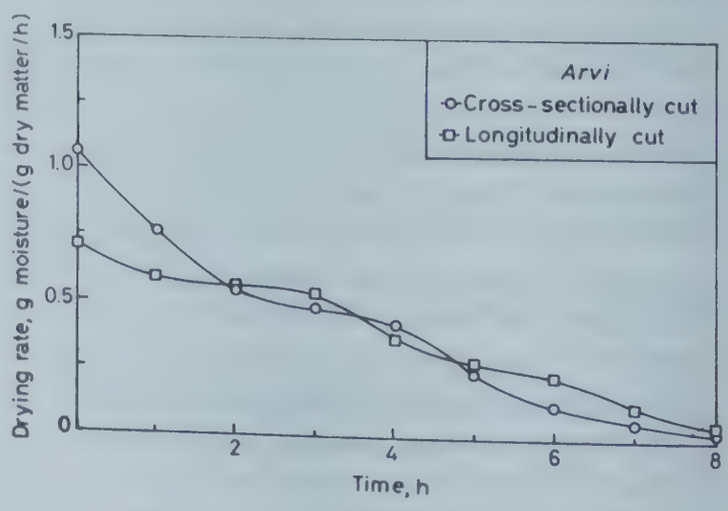


Fig. 1 — Drying rate curves for arvi (control)

cated that there was no constant rate period present and that for the entire duration the drying of arvi took place under the falling rate period. The drying rate is therefore accepted as being controlled by the rate of internal moisture movement, since the moisture content was below its critical moisture content.

Analytical models have been developed to describe the drying characteristics of particulate materials of regular shape[14,15]. The analytical solution to the diffusion equation, however, is not applicable to the particulate materials such as arvi which is irregular in shape. Simplified solutions have been widely used to determine the drying characteristics of the particulate materials in such cases[15]. The series solution of the diffusion equation may be written, as shown in Eq. (4).

$$MR = a_0 \exp(-b_0 t) + a_1 \exp(-b_1 t) + a_2 \exp(-b_2 t), \quad ...(4)$$

where, MR is moisture ratio, dimensionless,

$$MR = (m - m_e)/(m_o - m_e), \quad ... (5)$$

m – moisture content at any given instant t, per cent (dry basis), m_o – initial moisture content, per cent (dry basis), m_e - equilibrium moisture content, per cent (dry basis), t- time, h, a_i and b_i are coefficients ($i = 0, 1, 2, 3, \ldots\ldots n$).

Equilibrium moisture content, me, was computed using the relation proposed by Isaacs and Goudi[16]. For the present case, Isaacs and Goudi[16] equation for m_e is expressed as in Eq.(6).

$$m_e = (m_1 . m_3 - m_2^2) / (m_1 + m_3 - 2 m_2), \quad ... (6)$$

where m_1 – moisture content of arvi at 2 h, m_2 – moisture content of arvi at 8 h, and m_3 – moisture content of arvi at 5 h.

Using the drying data pertaining to the control sample in which the pieces were cut cross-sectionally the m_e value was computed to be 1.42 per cent (dry basis). This m_e value (1.42 per cent) was used in the evaluation of the moisture ratio (MR).

A simplified form of Eq. (4) is the one-term model also called the "logarithmic model",

$$MR = \exp(-k t), \quad ... (7)$$

where k is a coefficient also known as the rate constant /h.

Equation (7) was earlier used by many workers[3,15,17]. The logarithmic model, however, did not describe the drying kinetics of arvi, it underestimated the drying curve in the beginning and overestimated it in the later stages of drying.

An alternative approach to the analysis of the drying data is to use purely empirical relationships. One equation that has been widely used to describe drying behaviour of biological materials is the Page's equation[15, 18-20].

$$MR = \exp(-k t^n), \quad ... (8)$$

where n is a dimensionless coefficient. The linear form of Eq. (8) is:

$$\ln\{-\ln(MR)\} = \ln(k) + n \ln(t). \quad ... (9)$$

Linear regression of Eq. (8) was carried out using the least- squares technique and the coefficients were determined. The values of the coefficients are given in Table 1. The drying kinetics of arvi are shown in Figs (2-4). The solid lines represent the values as predicted by Eq. (8). As seen in Figs (2-4), the Page's equation described well the drying characteristics of arvi over a wide range of moisture content and pretreatments. The coefficient of correlation was greater than 95 per cent in all the cases.

Table 1 — Values of the coefficient of the Page's model [Eq. (8)]

Pretreatment	k, h-1	n	R^2, per cent
Control: CS	1.163	0.1943	98.7
Control: LS	1.565	0.3293	99.4
Water-blanched: CS	1.659	0.2802	98.2
Water-blanched: LS	2.046	0.386	97.4
KMS-blanched: CS	1.819	0.2912	97.0
KMS-blanched: LS	2.162	0.3608	95.2

Note : CS — cross-sectionally-cut sample, LS — longitudinally-cut sample

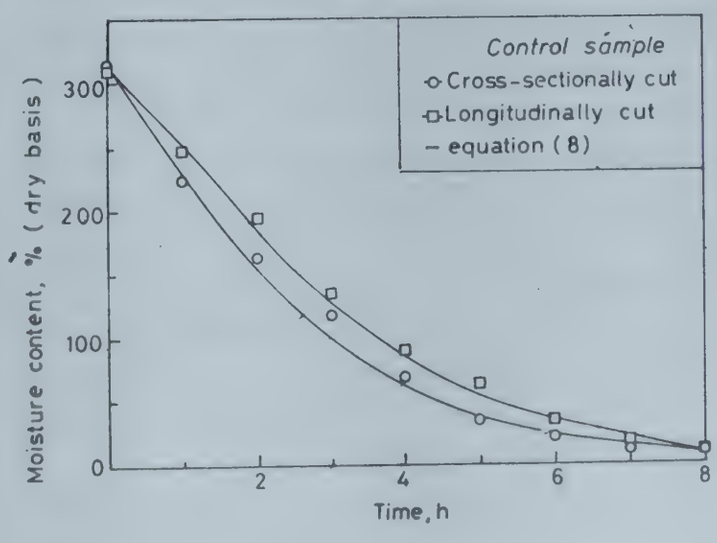


Fig. 2 — Drying behaviour of arvi (control) at 57 °C

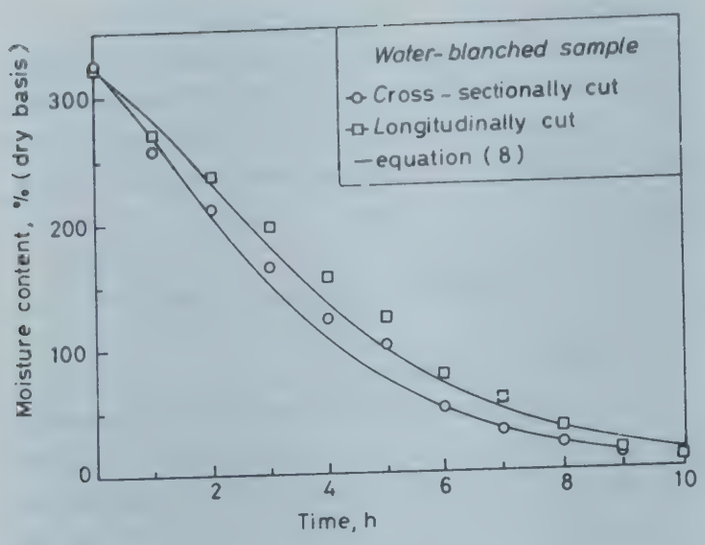


Fig. 3 — Drying behaviour of arvi (water- blanched) at 57 °C

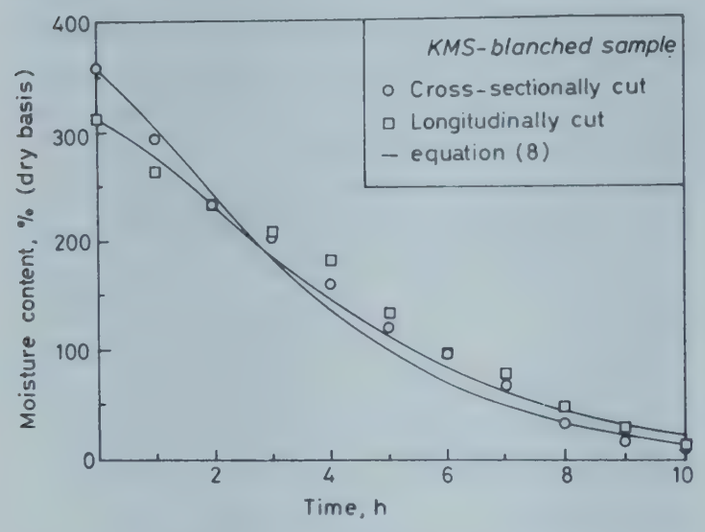


Fig. 4 — Drying behaviour of arvi (KMS-blanched) at 57 °C

Both the coefficients k and n of the Page's equation increased when arvi was blanched before drying. The reason for increase of the rate constant, k, with blanching pretreatment could be attributed to the fact that the blanching increased the moisture content and brought out changes at the physical and chemical levels, resulting in enhanced rate of drying. Both k and n were higher when arvi was cut longitudinally as compared to when it was cut cross-sectionally. The reason for such a behaviour is that the maximum distance through which moisture is required to travel from within to the surface of the material was lower in longitudinally cut samples.

For a dehydrated product to be made acceptable to the consumers, its quality attributes such as reconstitutability and overall acceptability must be comparable to that of the fresh material. The data on the dehydration ratio (*DR*), rehydration ratio (*RR*), and per cent reconstitutability (Table 2) revealed that the effects of pretreatments on the reconstitution characteristics was not substantial. Further the way the arvi was cut (cross- sectionally or longitudinally) also did not affect the reconstitution characteristics.

The evaluation of overall acceptability was based on the appearance, texture, and taste. The appearance was evaluated on the basis of dried product; while the taste and texture were based on reconstituted product. The average scores for the various pretreatments (Fig.5) demonstrated that KMS treated sample was preferred over the control and the water-blanched ones. Further, the judges rated the water-blanched dried arvi better than the untreated one.

Conclusions

Conclusions drawn on the basis of the results of this study are as follow:

(i) Drying of arvi takes place in the falling rate period,

(ii) The Page's model can be used to describe the drying behaviourr of arvi, and

Table 2 — Dehydration ratio (*DR*), rehydration ratio (*RR*) and per cent reconstitutability values for various samples

Parameter	Dried arvi	
	CS	LS
	Control	
DR	3.80	3.82
RR	2.24	2.26
Per cent reconstitution	58.9	59.1
	Water-blanched	
DR	3.84	3.89
RR	2.28	2.31
Per cent reconstitution	59.3	59.1
	KMS-blanched	
DR	4.89	4.03
RR	2.36	2.38
Per cent reconstitution	58.1	59.1

Note : CS — cross-sectionally-cut sample, LS — longitudinally-cut sample

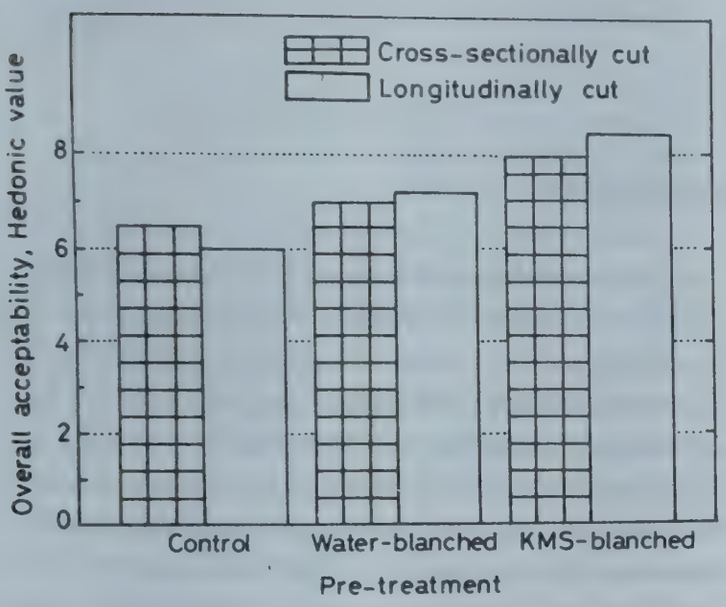


Fig. 5 — Effect of pretreatment on the overall acceptability of dried arvi

(iii) Arvi should preferably be water-blanched in boiling water for 2 min followed by treating in 0.5 per cent KMS solution for 2 min at room temperature.

References

1 Luhadia AP & Kulkarni PR, Dehydration of Green Chillies, *J Fd Sci Technol*, **15** (1978) 139-141.

2 Mazza G, Dehydration of Carrots, *J Fd Technol*, **18** (1983) 113- 123.

3 Mandhyan BL, Abroal CM & Tyagi HR, Dehydration Characteristics of Winter Vegetables, *J Fd Sci Technol*, **25** (1988) 20-22.

4 Chin HB & Dudek JA, in *Commercial Vegetable Processing*, edited by BS Luh and JE Woodroof (Reinhold Publication, USA), 1988.

5 Kumar S, Kalra R & Nath N, Dehydration of Bitter Gourd Rings, *J Fd Sci Technol*, **28**(1)(1989) 52-53.

6 Kanawade VL & Narain M, Effect of Pretreatment and Drying Air Temperature on Quality of Peas Dehydrated in Fluidized Bed Dryer, *J Fd Sci Technol*, **30** (1993) 118-120.

7 Mulay SV, Pawar VN, Thorat SS, Ghate UM & Ingle UM, Effect of Pretreatment on Quality of Dehydrated Cabbage, *Indian Fd Packer*, **5** (1994) 11-15.

8 Min Z & Schyvens E, Influence of Blanching Treatments on the Texture and Colour of Some Processed Vegetables and Fruits, *J Fd Proc Preserv*, **19** (1995) 451-465.

9 Vijayanand P, Chand N & Eipeson WE, Optimization of Osmotic Dehydration of Cauliflower, *J Fd Proc Preserv*, **19** (1995) 229-242.

10 Gupta A, *Influence of Size, Pretreatment and Air Temperature on the Drying Characteristics and Product Quality of Okra*, M Sc Thesis, Guru Nanak Dev University, Amritsar, India, 1996.

11 Ranganna S, *Handbook of Analysis and Quality Control for Fruit and Vegetable Products*, (Tata-McGraw Hill Publication, India) 1986.

12 Larmond E, *Laboratory Methods for Sensory Evaluation of Food*, (Department of Agriculture, Canada) 1977.

13 O'Neil PV, Advanced Engineering mathematics, (Wadsworth Publication USA) 1983.

14 Brooker DB, Bakker-Arkema FW & Hall CW, *Drying Cereal Grains*, (AVI Publication, USA) 1974.

15 Sharaf-Eldeen YI, Hamdy MY & Blaisdel JL, Falling Rate Drying of Fully Exposed Biological Materials: A Review of Mathematical Models, *ASAE Paper No. 79-6522*, 1979.

16 Isaacs WP & Gaudi AF, A Method for Determining Constants of First Order Reactions from Experimental Data, *Biotechnol Bioeng*, **10** (1968) 69.

17 Salek J, *Heat and Mass Transfer Studies in Fluidized Beds Combined with Microwaves for the Dehydration of Food Materials*, Ph D Thesis, University of Illinois at Urbana-Champaign, USA 1986.

18 Hutchinson D & Otten L, Thin-layer Air Drying of Soybeans and While Beans, *J Fd Technol*, **18**(4) (1983) 507-522.

19 Byler RK, Anderson CR & Brook RC, Statistical Methods in Thin Layer Par-boiled Rice Drying Models, *Trans ASAE*, **30**(2) (1987) 533- 538.

20 Shivhare US, Raghavan GSV, Bosisio RG, Mujumdar AS & van de Voort FR, Particulate Drying in Microwave Environment with Varying Initial Moisture Contents, *Powder Handling Process*, 3(2) (1991) 153-157.

Journal of Scientific & Industrial Research
Vol. 56, November 1997, pp 696 - 699

BOOK REVIEWS

The Dynamics of Technology, Trade and Growth, edited by Jan Fagerberg, Bart Verspagen, and Nick Von Tunzelmann (Edward Elgar Publishing Ltd, GL50 2HU, UK) pp 240, Price : £ 45.00
[ISBN 1 85278 922 0]

"Catching up" is undoubtedly the most contemporary concern in theoretical and policy economics. And what is not unusual is divergent approaches in the treatment of the problem in different theoretical traditions. Editors of this book, in their overview on The Economics of Convergence and Divergence, have presented an excellent review by tracing back the major points of emphasis in different theoretical traditions. The review draws our attention to the fact that the search for the measure of our ignorance has finally brought some convergence between mainstream and other heterodox economic research. But as editors suggest, there is still not much communication and interaction between economists with different theoretical background.

The volume under review is claimed to be a contribution to challenge this situation. It is definitely a beginning but not a very steady one in this direction. The neoclassical positions in the whole debate, the Kaldor-Myrdal insights, Baumels Convergence Controversy or Abramovitzs social capability are well known to the students and researchers in this area. Every individual contribution in the volume is an excellent addition to one or other theoretical background. And, of course, one gets all these contributions in one volume. But apart from that, so far establishing a thread of communication among various theoretical traditions is still elusive. The purpose, probably, could have been served better if the volume also included the discussions on each contribution. This was possible here since the book was the result of a conference. Presumably the papers have been presented in the conference, and put to discussion among the participants from different theoretical traditions.

Even in inclusion of more heterodox economic ideas, the volume is partial. Within the debate of catching up, in the realm of social capability there is a growing volume of literature, highlighting the role of skill, knowledge, and information. In fact, as Drucker says, in the post capitalist society, knowledge is going to be the only meaningful economic resource. The competitive edge, or the possibility of catching-up, according to this theoretical understanding, depends on the ability or disability of accessing, processing, and using information for generation of knowledge. Are we, therefore, entering into a new paradigm based on knowledge as the fundamental category after years of struggle with price competition and technological competition?

Closely related to this is the contribution from transaction cost economics which has brought in categories like organization, network, etc., from the other disciplines to the economic analysis. In this tradition, market is being conceptualized in a different way so much so that a market coordinated policy is considered as for laggards (a la Lazonick). Such an approach highlights the importance of economic policy and role of government and has the potentiality of bringing both the theoretical economics and economic management for catching up in the same platform.

The article by Reinert, however, takes up some of these issues to suggest the policies for Catching-up from way behind. What do others think about Reinerts arguments? This could have been the point of convergence of different economic backgrounds. India tried a similar policy through her initial five-yearly plans with indifferent achievements. Can the problem be located in economic management (through public sector enterprises)?

The book will definitely be useful for researchers in this area. But for the policy makers, in the absence of learned interaction on the issues raised by different

articles, there is no clue left on catching-up or convergence.

PRADOSH NATH
National Institute of Science Technology and Development Studies, New Delhi 110 012,India

Technology and International Trade, edited by J Fagerberg, P Hanson, L Lundberg and A Melchior (Edward Elgar Publish Ltd, Cheltenham, UK) 1997, pp 225, Price: £ 49.95.
BN 1 85898 528 5]

The last decade has witnessed significant changes in global trade patterns. The market shares of Japan and other fast-growing countries in Asia, like Singapore and Korea increased at the expense of other countries, while, at the same time, many European countries faced sluggish growth and increasing unemployment. Among the many factors affecting competitiveness and employment, many observers and science policy-makers have stressed on the importance of technology as the crucial factor in this context. For example, this view has strongly emerged in the recent science policy debates within the European Union.

The present book examines these issues in detail in order to understand the relationship between technology, competitiveness, trade, employment, and growth.

Chapters 1,2,3, and 4 focus on the fact that international competitiveness and market shares are mainly determined by R&D efforts, increased innovative activity and technological advantages. These chapters, basically, have the Ricardian or technology gap approach as the point of departure. While Fagerberg in Chapter 3, uses input measures, i.e., R&D expenditure, and other investments in new technology, Wolff in Chapter 1 and Gustavsson *et al.* in Chapter 2 focus on the output from these investments, as reflected in the total factor productivity(TFP). Verspagen and Wakelin, in Chapter 4, use both R&D and patents. In spite of these differences in data and methods, a common result is that the technological innovation, whether measured by R&D, patents or TFP, significantly increases competitiveness and influences specialization patterns. Furthermore, both Fagerberg and Verspagen and Wakelin find that although the estimated impact of R&D is larger in 'High-Tech' industries, but innovation also matters in many 'Low-tech' industries.

Theories that focus on 'economies of scale' as a source of competitive advantage, generally predict that with trading costs, large countries will have an advantage in industries where economies of scale are important.

Melchoir, in Chapter 5, examines the role of the domestic market size and provides evidence for its importance in competitiveness and for the role of proximity and trade flows for stimulating dispersion of new knowledge. He shows that in such a model the competitive advantage of a large home market will increase with the degree of product differentiation. Melchoir's empirical results also support the standard goods hypothesis suggested by Dreze in 1961 that small countries will specialize in homogeneous goods for which international demand is relatively standardized. He illustrates the need to take market structure into account when drawing conclusions about technology and specialization. This interplay between technology and the market needs more attention in future research since technology is always embedded in and shaped by the market.

Drud Hansen, in Chapter 6, analyses the consequences of technological progress in the form of learning for specialization. In a 'Ricardian' model analysed by Drud Hansen in which technical progress is a function of learning, history matters for competitiveness and original comparative advantage of the countries tends to be reinforced over time. This is in consistent with the fact that the specialization patterns of the developed countries tend to be rather stable over time, as shown by Wolff in Chapter 1. Drud Hansen concludes that once a country has obtained competitiveness in a sector, its competitiveness will be strengthened by accumulation of experience in the subsequent periods, and the trade pattern will therefore be preserved. He demonstrates that trade may increase the lead of the country that initially has the upper hand in the dynamic sectors.

Recently, the interest in technology as a source of trade and growth has been stimulated by the advent of the so-called new growth theory, combining the assumptions of economies of scale and imperfect competition with an explicit role for the firm in generating new technology. The traditional theory in this area only allowed for small and temporary effects of technology on the growth of increased trade. Dowrick, in Chapter 7, points out that the new growth

theories challenge this view. Following these theories increased openness may have permanent effects on growth. Further, trade may act as a direct transmission mechanism for the international dissemination of knowledge. The process of diffusion of new knowledge, as well as the notion of technological spillovers and their geographical reach are important for recent theorizing on the impact of technology on growth and trade.

Sjoholm, in Chapter 8, examines the impact of geographical proximity and contacts through trade on the dissemination of knowledge, using patent citation data as a measure of knowledge flows. He find that both trade flows and proximity have a strong positive impact on knowledge flows. New growth theory also stresses the importance of industrial R&D and its determinants for trade and growth. Countries that devote a large share of their resources in R&D will (considering that other parameters are equal) gain upper hand in high-tech industry. Further, if spillovers are national rather than global, the social returns to investment in R&D will be higher in large countries. The results reported here support the view that there is a strong geographical component to spillovers and knowledge flows in general. An important vehicle for overcoming such an obstacle is, of course, the Multinational Enterprise (MNE). If centres of technological excellence are widely dispersed and proximity is important for being able to share the progress that is generated, then MNE might find it useful to decentralize their R&D activities.

Globerman, in Chapter 9, examines the R&D strategies of MNEs and the extent to which these have changed recently. He finds that some decentralization has definitely occurred, though not for all MNEs. However, this also seems to be mainly in response to increasing internationalization and the need to adapt products in foreign markets.

Sorensen, in Chapter 10, and Honkatukia, in Chapter 11, analyze the factors affecting innovations in open economies. It is often agreed that R&D subsidies as well as tariff/export subsidies, promote economic growth. Sorensen investigates such interventions in a small open economy model where R&D and education compete for skilled manpower. He points out that draining the educational sector for qualified personnel may have detrimental consequences for the long-term performance of the economy. Honkatukia presents an open economy, monetary, R&D growth model. The main finding of the study is that inflation reduces R&D investments. This has the effect of reducing productivity growth, and thereby output growth, capital formation as well as marginal productivity of capital, independently of Tobin effect.

One of the reasons for the public interest in the technology competitiveness issue is the possible link with employment. The composition of employment has undergone considerable changes during the last few decades. In particular, the skill level in the labour force has risen. For example, the share of employees with higher education in Swedish manufacturing rose for 2.7 per cent in 1970 to 15.7 per cent in 1993 and a similar pattern can be seen in many OECD countries.

Chapter 12 dwells upon the impact of technology on labour markets. Here, Hansson finds that the increase of the average skill level of the Swedish industrial labour force reflects the increased use of skilled labour within firms, rather than a structural shift towards high skill sectors. He points out that skill based technical change seems to have been the most important factor. The tendency that industries characterized by high rates of innovation, adoption, and implementation of new technologies create the most opportunities for highly educated workers is thus an international phenomenon.

A basic conclusion derived from the work reported in this book is that technology plays a key role for competitiveness, and that its importance may very well by increasing, since many other factors such as physical and capital will probably become increasingly mobile. The results indicate that domestic innovative activity is still a major determinant of international competitiveness and that geographical proximity seems to be important for the diffusion of knowledge.

Chapters presented in the book are well-written and nicely presented. The book is of definite interest to academics and policy makers, particularly those in the field of international trade, economic growth, industrial organizations, and technology management.

V P KHARBANDA
National Institute of Science, Technology
and Development Studies,
New Delhi 110 012, India

International Year Book of Industrial Statistics, (UNIDO, Vienna Edward Elgar Publishing Ltd, Hants, UK) 1996, pp 648, Price: £ 99.95
[ISBN 185898 471 8]

The UNIDO has maintained continuity by publishing the Year Book for 1996 providing comparative statistics on current performance and trends in the manufacturing sector worldwide. Updates on the data types and covering gaps in certain cases are normal practices in case of such publications. The 1996 issue of the year book has certain countries not included in the earlier issues. Exclusion of certain countries, like Afganisthan, is understandable. But it is not so for all exclusions. An editorial note on exclusions and inclusions would have been useful.

In my review of the 1995 issue, I had raised the question of standardized definition and concepts of various indicators used in the volume to make inter-country comparison of such indicators possible. It is probably a necessity in the age of globalization. UNIDO is definitely the appropriate agency for this task. Hope, UNIDO would take up the matter in the future edition.

PRADOSH NATH
National Institute of Science, Technology and Development Studies, New Delhi 110 102, India

Journal of Scientific & Industrial Research
Vol. 56, November 1997, pp 700 - 716

SCI-TECH UPDATE

UNEP-OzonAction Programme—A new software released

United Nations Environment Programme's Industry and Environment (UNEPIE) Centre has just released a new software "OzonAction Information Clearinghouse Diskette Version 5.0 (OAIC-DV) as a part of their services to combat ozone depletion. It is the first time when the diskette has been made available on Windows™ format. This diskette contains information on environmentally safe "Ozone-friendly" technologies and expertise from different organizations and individuals that have experience in successfully phasing out ozone depleting substances (ODS). It would serve as a reference tool for their counterparts in developing countries who are interested in such technologies and expertise as would help them in their transition to non-ODS alternatives.

The production and use of CFCs and some other substances that deplete the ozone layer are controlled under the Montreal Protocol Treaty (1987). The use of ODS is to be reduced under phased programmes by different countries. Worldwide information exchange has been accorded high priority under the Protocol to expedite industrial conversion to eliminate ODS use. Accordingly, UNEP's role as a Implementing Agency includes providing information clearing house services to assist the technology transfer process between industries in developed and developing countries and the production of this diskette is a big step in that direction.

For additional information, contact

Mr Rajendra Shende
Four Mirabeau
39-43 quai Andre Citroein
75739 Paris Cecex 15
France
or find at web site
http://www.unepie.org/ozonaction/html
[*Development Alternatives Newslett*, 7 (No. 7) (1997) 5]. ❑

BSA

Microprocessor controlled filter reduces vehicular pollution

Old diesel engines are a major source of vehicular pollution on roads as they emit carbon monoxide and nitrogen oxides alongwith particles of unburnt fuel and soot. Lower sulphur diesel fuel coupled with a catalytic particulate trap fitted to the exhaust pipe offers one solution to tide over the problem. but low sulphur diesel is costly and the traps are still more costly. Also this combination is more effective for new vehicles with little wear in their parts.

Hassan Assali, a London motor-engineering consultant has come up with a cheaper way to clean up the exhaust from diesel engines. According to him, the pollution is caused more by the lubricating oil which tends to seep through the gap between worn pistons and cylinder walls. The lighter fractions of the lubricating oil leaks more easily into the combustion chamber. The lubricating oil contains minerals like Ca, Mn, Ba and Zn. this causes a sludge of the left out oil and the minerals shoot out of the exhaust pipe, adding to the pollution.

Assali's solution to this problem is to filter the oil. His company has devised a filter called Pinmore electronic oil- recycler to carry out this job. The new filter contains, in addition to the conventional filter-cartridge, a secondary filter controlled by a microprocessor. It consists of a pyramid of stainless-steel discs, through which the oil cascades. An element at the top of the pyramid heats the discs of 160°C and they bring the oil to a temperature of 120°C—some 40°C hotter than its normal temperature in the engine. As the oil trickles down, the light fractions along with contaminants evaporate, and the resultant vapour is fed back round into the fuel inlet and there to the combustion chamber where it is consumed. Without the light fractions, the minerals in the oil stay behind and keep it clean and slippery for longer. It is claimed that a very old bus can run for as much as 60,000 km without an oil change.

Two British operators have tried out the Pinmore filter for the last two years and pronounced it to be successful. The filters are going to be mass produced in China and may cost around $ 500. The filter's main attraction is economics and environmentalism marching hand in hand [*The Econ*, 23 November, 1996, p. 111]. ❑

DSRM

Microelectronic device implant to stimulate nerves

Two researchers, Dr Nicholas Donaldson, and Tim Perkins have developed microelectronic assemblies that can be implant into patients to stimulate the nerves in their backs below the point of injury.

The microelectronic implant was studied on Ms Julie Hill who suffered a fracture of her spinal cord in a car accident, leaving her paralysed. Stimulation of nerves in such injuries helps the patients to reduce the danger of pressure sores and bladder infections.

The device consists of a receiver placed under the skin next to the ribs and wires that feed around to the back of to electrodes that lie on six pairs of nerve roots. Power and appropriate signals are fed to the simulator using rf induction.

The patient was tested once a week during which the nerves in her back are electronically stimulated and the effect on leg muscles was recorded. Her performance was found to improve over time as she recovered from surgery and her muscles grew in strength. The research team will continue their simulation studies to enable them to see that this can give greater control over the legs and the bladder [*Spectrum, Brit Sci News*, November/December 1996, p. 18]. ❑

DSRM

New microscopic semiconductor crystals for basic research

Researchers at the Weizmann Institute have shown that by manipulating the mismatch between the spacing of atoms in two materials they can control the size of microscopic semiconductor crystals. This will help in development of tiny semiconductors with new optoelectronic properties for basic research and for tomorrow's optics and electronics industries because the properties of crystals smaller than approximately 10 nm, can be altered by merely changing their dimensions.

This research was conducted by Dr Gary Hodes, Prof Israel Rubinstein and then doctoral student Yuval Golan, all of the Materials and Interfaces Department.

Using a technique called electro-deposition, the scientists laid down crystals of the semiconductor cadmium selenide, each measuring 4-5 nm onto a gold substrate. The crystals were found to be oriented in a uniform manner. This configuration is highly beneficial for controlling the semiconductor properties and it occurs because the atoms of the crystals tend to align themselves with the atoms in the surface layer of the substrate. Such alignment is attributed to the good match between the interatomic spacings of cadmium selenide crystals and of gold.

According to Hodes, it is the small remaining mismatch that allows for precise control over crystal size. The substrate "Stretches" the growing crystal in an attempt to minimize the mismatch, creating a strain within the crystal that eventually causes it to stop growing altogether. Therefore, by fine-tuning the mismatch the scientists were able to determine when the crystal will stop growing, in other words, its size. It was also found that the addition of small amounts of tellurium to the semiconductor reduced the mismatch to a predictable degree. This allows to produce uniformly oriented crystals of varying sizes. Compared with alternative approaches, this method is claimed to be much simpler and cheaper and makes it possible to control the size of smaller crystals [*Sci Tips*, Weizmann Institute of Science Rehovot **2** (3) (1997)]. ❑

DSRM

Diamond films grown in Space

A thin film of diamond was successfully synthesised during the last flight of Space Flyer Unit, an unmanned experimental space laboratory, according to Japan National Space Development Agency.

Because of their optical and electrical properties of diamond, there is a great demand for them. The data obtained from the space Flyer during this synthesis is known to be the first one of such a study conducted in a microgravity environment. The results obtained in this experiment will be of significant help in the efforts to make diamond films on Earth where gravity can create convection currents that influence the quality of the material.

In the experimental space laboratory the diamond thin films were grown on a substrate by reacting methane gas and hydrogen gas together in high energy conditions. In this chemical - vapour phase-growth method, carbon from methane gas form deposits of diamond grow on substrate. After recovering the Flyer, scientists analysed the substrate and found the diamond thin film with a thickness of 0.01 cm and a diameter of 4 mm. It is believed that the chemical-vapour phase method of crystal growth promises to be a better way of mass producing diamond thin films than the conventional method which requires high temperatures and pressures [*Opt Laser Technol*, **29**(1)(1997)(vii). ❑

DSRM

Hitech scanner that reads aloud

Olympus Opticals have developed an altogether new Scanner which unlike the conventional ones reads aloud for the user. This high- tech scanner will prove useful for the visually improved propel as an alternative to Braille reading and writing.

Called Scantalk, the new scanner converts spoken language into a digital code which can then be printed on paper and "read" with a hand held scanner that converts the code back into sound. In its operation, the reader runs a pen sized scanner lightly across a line of code. A red light-emitting diode reflects the light from the page to a CCD video pick up and a small computer converts the code into sound. The user can listen to the text through ear phones, fitted to scantalk or through an auxiliary audio system. The scanner can also be used to digitize written characters and images which can then be printed, downloaded onto a computer, or displayed on video. The digital code is printed in tiny blocks (2.1 mm^2) with positions for thousand black dots. By aligning these blocks of code on a page Scantalk can record, store, and print significantly greater amount of data than conventional print methods. An 8.4mm X 100 strip of the digital code for example can hold up to 15 s of sound or 256 X 256 pixels of colour image. The digital code allows a great deal of freedom in the layout process and can be reproduced through offset printing. Two AA batteries used in Scantalk last for about 5 h. The same is also equipped with error correctional capabilities to ensure that hearing is not impaired by specks or minor strains on the paper. Olympus may market this product in the first half of 1997 along with coded children books and English language practice materials. The company can be contacted for further information at 81-426-42-0051 [*Look Japan*, **42**(410)(1997)25]. ❑

DSRM

Method for dust fingerprinting

Airborne minerals are major contributors to the dust flux nd their physico-chemical characteristics are of scientific interest and have a direct bearing on environmental health issues. Earlier work on R&D in this direction was not focussed on assessing the qualitative characterization of aeolin dust for air quality monitoring in impact assessment and regulation.

The Earth Resources Centre (ERC) at Exeter University has established a research programme at Ffos Las opencast coal site on southwales to 'fingerprint' dust. During this programme, dust from the airborne flux, and dust deposited in localities adjacent to the opencast coal-workings was collected and analyzed.

The analysis consisted of X-ray diffraction for qualitative analysis of mineral species and Scanning Electron Microscopy (SEM) to obtain a photographic record and estimation of particle size and shape, along with Energy Dispersive Analysis to determine their chemistry with the technology established, Eighteen months of monitoring was done in order to establish a database of dust and test its value. The mineralogical data were examined using the GIS package ARC INFO. Analysis of data showed that some minerals such as calcite reflected a regional input of dust to the airborne flux, and, that, increased clay minerals could indicate disturbance of material due to overburdened storage and haulroad input from the local opencast mine. The concept of dust fingerprinting was established from the clay to non-clay relationships coupled together with particle-size information. All this earlier work was further developed in order to assess the contributions of industry through fly-ash captured on SEM images and organic particles from diesel emissions. Filter samples from personal and high volume samplers have been analyzed and a programme of work is further undertaken using the Tapered element Oscillating Microbalance (TEOM) developed by Ruppreckt & Patshnick using space technology.

Local authorities and mining companies in UK are also setting up their own dust monitoring programmes using commercially available British frisbee deposit gauges and incorporate them into environmental control and regulatory process.

With the dust fingerprinting techniques, it is now possible to provide scientific proof of the origin and nature of dust escaping from industrial processes. Successful applications include opencast mine workings, road-building schemes and particulate emissions from steel works [*Spectrum*, British Science News, No 255, November/December 1996]. ❑

DSRM

Shrinking sensor technology

Hans Biebuyck *et al.* at the IBM Research Laboratory in Zurich, Switzerland have devised an elegant method for immobilizing several ligands onto a surface simultaneously, with potential use in various miniaturized applications, ranging from bio-sensors and immunoassays to combinatorial screening assays [*Science*, **276**(1997)779-781]. The method used a pre-molded poly- dimethylsiloxane (PDS) make imprinted with a network of channels. The PDS mask is first placed onto the 'sensor' surface to create a network of microchannels (3 mm long and 3 μm wide) into which nonliter quantities of reagent are drawn by capillary action. Once proteins in the reagent have bound to the chemically activated surface, the PDS mask is removed, and the resulting exposed areas are blocked to prevent non-specific protein binding. The fluorescence microscopy studies also reveal that attached IgGs remain structurally intact and that different IgGs can be added to respective channels simultaneously. The format is found to be amenable to enzyme - linked immunosorbent assay (ELISA) - type tests and it is simple, inexpensive and economic of reagents and applicable to miniaturization of many assay formats being currently used. [*Nature Biotech*, **15**(6)(1997)p.492]. ❑

HSDK

Engineering ideal trees for the paper and pulp industry

According to the scientist John Ralph of the Department of Agriculture Research Service in Madison, Wisconsin, a mutant pine tree from North Carolina could help genetic engineers to develop ideal trees for the paper and pulp industry, because its lignin can be removed more easily. Removing lignin is the basis of pulping, the process by which wood and plant fibres are turned into paper and cardboard. It made possible for genetic engineers to modify lignin compositions so that they are more easily removed without killing the trees.

The mutant tree has a very low level of coniferyl alcohol-based lignin. But, it successfully uses two alternative base molecules, dihydroconiferyl alcohol and methoxybenzaldehyde to form perfectly serviceable lignin (*Science*,**247**(1997),235). According to the view of lignin biochemists, trees follow a very strict lignin recipe. The mutant loblolly pine, however, shows that trees can make lignin out of almost anything. According to Ralph, this tree can make changes to lignin composition way beyond what was considered possible. Modified trees could also have other uses. For example, it may be possible to genetically engineer, a tree that uses styrene monomer as its lignin precursor. Instead of wood, the tree trunk would then be made of polystyrene [*Chem Ind*, (**No. 14**) (1997), p. 543]. ❑

HSDK

A novel catalyst for non-radical molecular oxygen activation reported

Metal catalyzed oxidation of organic compounds with molecular oxygen almost always takes place by a free-radical mechanism. Ronny Neumann and Mazal Dahan of the Hebrew University of Jerusalem, Israel, have recently reported a ruthenium-substituted poly-oxometalate that activates molecular oxygen through formation of an intermediate ruthenium-oxygen species which is capable of selective alkene epoxidation. This inorganic cluster acts rather like a dioxygenase enzyme, and might provide a robust catalyst for industrially important oxidations.

According to Hill and Weinstock [*News & Views, Nature*, **388** (1997) 332-333], an ideal homogeneous catalyst for dioxygen (O_2) oxidations would be selective, useful for a variety of substrates and chemical structures, reasonably fast, and stable. And specifically for the use of O_2, the process should not require the wasteful addition of reducing agents. Such a system has remained a dream, but the work of Neumann and Dahan is a big step towards realizing this goal.

The Neumann-Dahan catalyst, $\{[WZnRu_2(OH)(H_2O)](ZnW_9O_{34})_2\}^{11-}$, contains two sterically protected ruthenium atoms sandwiched between $\{ZnW_9O_{34}\}^{12-}$ halves of the oxidatively resistant poly-oxometalate. The catalyst facilitates direct O_2 activation and substrate oxidation without generating non-selective radicals. Oxygen is incorporated directly into the substrate, the sole source of the electrons needed for the reductive activation of O_2. They have proposed that dioxygen activation as shown in Eq.(1), occurs. This may or may not be followed by a disproportionation reaction as shown in Eq.(2).

$$Ru^{II} + O_2 \longrightarrow [Ru^{III} - O - O - Ru^{III}] \longrightarrow 2Ru^{IV} = O \quad \ldots (1)$$

$$2Ru^{IV} = O \longrightarrow Ru^{II} + O = Ru^{VI} = O \quad \ldots (2)$$

According to Neumann and Dahan, the polyoxometalate can be considered to act as an inorganic dioxygenase catalyst. The advantage of using inorganic catalyst such as polyoxometalates, as compared to organometallic complexes, is their well-documented stability against decomposition of self-oxidation.

Hill and Weinstock feel that challenges now are to achieve broader applicability (of course, only to hydrocarbons), faster reaction rates and compatibility with a range of reaction conditions [*Nature, Lond*, **388** (1997) 353-355]. ❑

BSA

Assessing corrosion in cementitious structures by using NMR

Chloride - induced reinforcement corrosion in cementitious structures is a complicated problem, the scale of which is affected by numerous influence ranging from the cover to reinforcement, degree of pore saturation, and the nature of the binder used. The microstructure of portland cement paste is complex and is affected by a wide variety of influences including type of binder, water/binder ratio and curing. The capillary pores in the paste phase have a controlling effect on the overall durability of concrete because they are the primary source of mobility of fluids and dissolved ions.

The problem is complicated because the concrete cover is not inert and is one that changes with time and in its ability to bind chemically with ions such as chlorides. A great deal of effort has been directed towards characterising the hydrate phase. But most conventional techniques suffer from the problem that they are both intrusive and perturbative to the underlying structure. For these reasons, techniques that can assess the physical and chemical nature of the hydrate and pore structures non-destructively are useful. Magnetic Resonance Imaging (MRI) technique has been established as a non-invasive diagnostic technique. The method maps the processional frequency of hydrogen nuclei in a magnetic field after application of a radio frequency pulse and magnetic field gradient. The related technique of Magnetic Resonance Micro-imaging (or Microscopy) (MRM) has also been developed for micrometer-resolution studies with much smaller samples up to about 20 mm diameter.

The MRI techniques of Stray Field Imaging (STRAFI) and Gradient- Echo imaging are being developed which make possible the spatial mapping of water and organic molecules in concrete. in addition to ^1H, cements and concretes contain other nuclei such as ^{27}Al and ^{29}Si with non-zero nuclear spins. Chlorine also has two isotopes with non-zero number spins, ^{35}Cl and ^{37}Cl. Nuclear Magnetic Resonance (NMR) spectroscopy can provide information about the chemical state of these elements. The quadrupolar interactions can be averaged to their isotropic values by the technique of magic angle spinning (MAS) in which the sample is spun at high rotational speed about the magic angle of 54 degrees 44 minutes to the spectrometer magnetic field direction. Several MRI methods have been developed to overcome broad resonance lines and thus permit high spatial resolution imaging of solids and combined liquids.

MRI techniques offer a novel way of non-invasively establishing the kinetics of water mobility in Portland cement-based systems and through MAS spectroscopy the underlying chemical environment of the hydrate structure and how this can affect diffusing ions such as chlorides.

For more information, contact:

Department of Civil Engineering
University of Dundee
Dundee, Scotland DD1 4 H N, UK
Tel: 1382 344343
Fax: 1382 3444816
E-mail: mrjones @ dundee.ac.uk.

[*Chem Week*,**42**(No 50)(1997)p.130]. ❑ HSDK

Catching speeding electrons in a circuit city

Jeffray Kash et al. at the IBM Thomas J. Watson Research Centre in Yorktown Heights, New York, obtained an aerial photograph of the city at night and observed the traffic pattern traced in the bright streams and dense clusters of car headlights the equivalent shot of a functioning microprocessor, the 1997 S/390, used in the current generation of IBM mainframes. By directly viewing such traffic patterns, which consists of electrons emitting light as they pass through the transistors or cross roads, circuit designer can look for weak spots and bottlenecks in the millions of components on a chip.

The electrons emit light as they pass through the field-effect transistors [FETs] at the heart of most modern microchips. The light, which is in near infrared and is extremely weak, can be detected only with cooled charge-coupled devices or special photomultipliar imaging tubes. Kash et al. investigated this particular microprocessor because it consumed two orders of magnitude more current than it should have when it was not performing any operations. They obtained the images of the chip in this 'quiescent' state which showed a series of spots indicating that this excessive current was confined to a small portion of the chip. They couldn't tell which of the 7.8 million transistors were at fault because individual transistors in their images couldn't be identified.

The problem was solved by spying on the individual FETs as they shuttled electrons around the chip when it was operating normally. The FETs produce picosecond light pulses as they switch on and off, so by photographing the chip in normal operation, Kash *et al.* obtained a road map of the positions of the FETs. When this image was superimposed on the photo showing the excess leak currents, they pinpointed exactly where the leaks occur.

The technique is useful because one can look at hundreds of thousands of FETs on a chip which is very helpful in improving the design of subsequent chips. According to Ingrid De Wolf of IMEC Belgium's Inter-university Microelectronics Centre in Leuven, the optical - emission diagnosis of chips is beginning to spread throughout the microelectronics industry. She is hopeful to get more information from the spectrum of the emitted light, so that the energy of the electrons can be measured [*Science*, **276** (No 5321) (1997) p 1987]. ❑ HSDK

Use of twist principle in semiconductors

Ejeckam *et al.* have invented a substrate that doesn't require lattice matching a universal substrate which is very useful for the optoelectronics industry. When an epitanial layer is grown on a substrate with a different lattice parameter, at first the growing layer elastically distorts itself to fit the crystal matrix so that the lattice planes are continuous across the interface. When a certain critical thickness is exceeded, the elastic energy is released by plastic deformation, in the form of dislocations which nucleate at the surface and then travel into the interface. A dislocation is a boundary between part of a crystal that has slipped and part that hasn't. As it moves through the crystal it displaces one row of atoms at a time, on reaching the far side it has displaced an entire layer. The energy barrier to this process is much lower than it would be for all the rows of atoms to move at once.

One approach to the problem is to make the substrate very thin, so extending the critical thickness by showing the strain between the substrate and overlayer. These structures are extremely fragile, too fragile to withstand normal wafer handling and processing.

Dislocations are usually detrimental to device performance put Ejeckam *et al.* have put them to work to make a stretchy universal substrate. A film of gallium arsenide (GaAs), only 30 Å thick, is grown on an ordinary GaAs substrate with an aluminium arsenide (AlAs) spacer layer in between, then the thin film is bonded to another substrate together at high temperature. After fusing the surface together, the original GaAs substrate and the AlAs are removed with selective chemical etches.

The universal substrate works on twist boundary. This is created by rotating the thin film before fusing it to the substrate, introducing an angular misalignment between the directions of the two lattices. A grid of screw dislocations exists in the plane of the interface to accommodate the twist. At the cores of the dislocations the atomic bonds are stretched.

Ejeckam *et al.* first grew, InGaP on a universal substrate. The lattice mismatch was 1%, yet they were able to grow a layer 3,000 Å thick without defects- 30 times the critical thickness. Then they,

tried growing gallium antimonide (GaSb). The lattice constant of GaSb is 6.096 Å, whereas that of GaAs is 5.653 Å-a strain of 8%. Under ordinary conditions defects would start to invade the perfect crystal after four or five manolayers had been grown. But the 3,000 Å layer of GaSb grown on a universal substrate is defect-free, despite being more than 300 times the critical thickness.

A universal substrate made of silicon would be useful because it conducts electricity well. GaAs is the most widely used synthetic semiconductor and is also an efficient light emitter. Indium antimonide (InSb) is found to be capable of both functions. It is luminescent and has electron and hole mobilities many times better than silicon. The lattice mismatch between InSb and GaAs is 15%, and its critical thickness is less than a manolayer. A 6,500 Å- thick, dislocation free layer of InSb has been grown for the first time, on a universal substrate [*Nature*, **388** (No. 6637) (1997), p 29]. ❑

HSDK

Transforming household wastes into useful materials!

If the research findings of a group comprising Pascale Colombel and her guide Nicole Godon at the French Atomic Energy Commission (CEA), Marcoule, France, take a practical shape, then an ideal solution would become available for managing household wastes by transforming them into new raw materials.

A general practice followed for destroying household wastes is burning. But even after burning, these wastes remain toxic. The ashes are full of heavy metals, like aluminium and silica, and other harmful materials. The solution put forward by these researchers is to transform these ashes into glass which could be used for many useful applications including road building.

According to these researchers the presence of silica and aluminium in these toxic wastes make them perfect for vitrification. They have found that if these ashes are melted with a plasma torch and cooled subsequently, they form a solid material. The toxic elements are trapped inside either directly through chemical link or in the form of small crystals with a very low solubility. However, it remains to be seen if this new material is indeed environment-friendly and how long it will remain so. These researchers postulate that the new material would remain harmless over several thousands of years.

These researchers have conducted their study under five different stages — characterisation of new material, defining their potential applications, finding parameters that may influence the release of toxic elements into the environment, determining durability of the material through modelling, and finally testing the effect of the material on environment. These researchers have found that a material measuring 10 cm^3 sideways subjected to pure river water would have a minimum life time of 2,700 years. The release of toxic elements into river water is very slow due to which their concentrations remain much below the limits prescribed for drinking water.

These researchers opine that the solids created from household wastes could be extremely useful owing to their various qualities. "However, much depends firstly on the approval by the government and secondly on the acceptability by the people", feel the French duo [*Technical News, Centre for Documentation on Universities, Science and Technology* (Embassy of France, New Delhi), No. 11, June 1997. ❑

BSA

Ecotaxes help in abating pollution—finds OECD report

According to a report entitled "Evaluating Economic Instruments for Environmental Policy", brought out by Organization for Economic Cooperation & Development (OECD), the environmental taxes and other economic instruments have helped in reducing pollution, although they were initially not designed as revenue collectors. These charges, taxes, and tradeable permits are not merely being absorbed as a cost by polluters but are acting as incentives to improve environmental quality, says the report. Although unanticipated, these economic tools have forced governments and/or their environmental agencies to develop better measuring and monitoring systems. As a result, these entities now have the information needed for better enforcement of regulatory policies.

It may be mentioned here that to combat pollution some countries had introduced 'Taxing System' for polluters. Some of them have even declared pollution as a 'tradeable commodity'. Consequently, industrialized countries of OECD — including the US —

have increasingly employed fiscal instruments to curb pollution during the past ten years. However, few studies have evaluated the cost and benefit effect of these measures. It is in this context that this report of OECD has gained a significant value.

Some of the specific cases mentioned in the OECD report are as follows:

In 1970, the Netherlands introduced a water pollution charge to finance treatment of wastewater from homes and industry. An unintended benefit of revenue-producing tax has been cut-backs in discharges of heavy metals and other pollutants despite tremendous economic growth in the country. Similar results have been noticed in France and Germany.

Some cities in the US — High Bridge NJ., and Pekasie, Pa, for example — have instituted "pay-per-bag" refuse collection charges as revenue generating mechanisms. As a result, the amount of house-hold solid waste being sent to landfills has declined, as recycling has increased.

According to Alexander Cristofaro, deputy director of the Environmental Protection Agency's Office of Policy Development, the OECD document describes 'all economic instruments used in industrialized countries. Its greatest value will be to "countries in transition", who would take advantage of the experiences of other countries and would be able to choose the best for them' [*Chem Eng News*, **75** (No. 22) (1997) p. 8-9]. ❑

BSA

A process for growing cotton plants producing cotton/polyester hybrid fibres developed

Researchers at the Agracetus, Wisconsin, USA have developed a process for growing cotton plants which produce cotton/polyester hybrid fibres. It is for the first time cotton fibre has been modified usefully through genetic engineering.

They used the bacterium *Alicaligenes eutropus*, a widespread natural producer of plastic which is completely biodegradable. Grown in a carbon-rich environment, the bacterium stores excess carbon by forming minute carbon-rich granules of a polyester: poly-hydroxybutyrate (PHB). Whenever required, these granules are broken down naturally by bacterial enzymes, releasing the carbon.

In somewhat tedious process, genes isolated from the bacterium, but still containing three enzymes vital for producing PHB, were introduced into cells of cotton seedlings. The plastic production process, when the transgenic process was successful, became part of the cotton plant's metabolism. By judicious pruning, as plants were grown from the seedlings, the researchers were able to cultivate a limited number of mature cotton plants possessing at least one layer of genetically transformed tissue along their entire length. These plants maintained normal growth rates and other performance. The cotton/polyester fibres from the plants combine the normal handle of cotton with better thermal insulation properties.

The further long-term development will be targeted towards growing, on a large yet economic scale, longer thickness fibres of this type which are less crimped to improve easy-care performance. It may even be possible to grow inherently coloured fibres to circumvent a need for drying when, e.g., they are to be used in jeans [*Tech Text*, **8** (No. 3) (1997) p. 32]. ❑

HKK

Sorbent products for industry

New Pig Corp, USA, has developed several hundred contained- sorbent products for use in various industrial environments.

The company's product known as the Pig Absorbent Sock, which could be shaped around a machine, was launched in the mix-80s. New Pig's 227-page product catalogue features a comprehensive range of disposable and reusable sorbent containers, kits, socks, pillows, pads, and mats, based on needle-bonded, spun-bonded and melt-blown materials, speciality fibres and various sorbents.

The products are employed in clearing oil from ocean, lake and river spills, and more routine cleaning of everyday leaks and spills in factories or during transportation. In addition to oil sorbent products, others are supplied for mopping up various liquids such as water, acids and alkalies [*Tech Text Int*, **8** (No. 3) (1997) p. 32]. ❑

HKK

Emulsion incorporates liquid crystal

A team led by David A Weitz at the University of Pennsylvania, using a liquid crystal as the solvent phase has prepared stable emulsion that exhibits novel colloidal interactions. The work opens the way to a new field of emulsions that use anisotropic fluids.

They prepared the emulsion from water and the nematic liquid crystals are made up of rod-shaped molecules oriented lengthwise along a common axis called the director. The emulsion comprises drops of the nematic fluid as large as 50μ in diam that were themselves dispersed in a water phase. Dispersed within the nematic drops were water droplets 1 to 5μ in diam.

The mixed emulsion remained stable for several weeks. The stability of the droplets was derived from the anisotropic nematic fluid. When heated so that the rod-shaped molecules became randomly oriented, the water droplets became unstable and coalesced.

Because liquid crystals rotate a plane of polarized light, they can be distinguished from water and other isotropic fluids by cross-polarization techniques. Using this approach, the Penn researchers showed that virtually all of the nematic drops contained smaller water droplets. The encapsulated droplets always formed chains that were located preferentially at the center of the nematic drop. Droplets in a chain were markedly separated from each other. The chains broke when the solvent was heated.

The anisotropic liquid crystal was concluded to have two effects: It induces an attractive interaction between the water droplets that leads to the chaining, and it causes a short-range repulsive interaction that separates the droplets.

To help explain how these effects come about, the researchers compared the cross-polarization patterns produced by a nematic host containing one water droplet with those produced by hosts that contained two or more droplets. It was concluded that the water droplets create defects in the host fluid by distorting the orientation of the nematic director. The defects prevent close contact between the droplets and give rise to a long-range attraction between them.

These emulsions might have applications in the cosmetics, agriculture, and drug industries. More immediate applications might be in polymer disperse liquid-crystal displays or in optical switches [*Chem Eng News*, **75** (No. 12) (1997) p. 11 and 12]. ❑

HKK

Machine that 'prints' tablets to order developed

Researchers at the Massachusetts Institute of Technology (MIT) have made complex controlled-release patients tablets, specifically tailored to a patient's need, using equipment very similar to the inkjet printer on computer. They have combined together concepts employed by researchers in rapid prototyping and the computer industry's inkjet workhorse to develop a machine that 'prints' tablets to order.

Earlier, MIT workers Michael Cima and Emanuel Sachs developed a 3- 'printing' technology to make solid ceramics with intricate designs. In their equipment, a continuous spray head rasters in the X and y directions across a bed of power about 100-150 r m deep. The computer-controlled spray head delivers a binder chemical to the powder where it is not needed an electrostatic device diverts the stream of binder into a dump. When a layer has been treated in this way, the powder bed is ratcheted down and a new bed of powder blown across it, ready for the next layer to be built up. When the process is over, all the unbound powder is blown out of the piece, which is ready for firing. Such intricate ceramics are used as moulds for casting metallic parts for cars, aircraft, or medical implants.

Now Cima and Robert Palazzolo have teamed up with Ben Wu of Harvard School of Dental Medicine and William Rowe of Therics, a Princeton-based pharmaceutical company who have been extending the 3-*D* technique to 'print' pills, which are also made up of powder and binder. Even complex pills can be envisaged with this technique, e.g., the pill could consist of many concentric layers which would release a drug as the tablet slowly dissolves in the stomach, or it could contain a precisely formulated work-tail of different drugs.

The key change to the 3-*D* technique has been to replace the continuous spray head (which is wasteful of expensive pharmaceutical product) with a head that only fires when required ('drop on demand'). The inkjet or bubblejet printer provides the model, where a sudden burst of electric current vapourises a tiny amount of the liquid ink, forming a bubble that explodes onto the paper. Replace the paper with the powder bed of Cima's 3-*D* machine, and replace ink with a drug solution, and you have a pill printer.

The team had to prove that the treatment does degrade the drug. For this, they took a product that is known to be the heat- unstable, epinephrine, and put that through the process. Epinephrine is significantly degraded within 1 min at 60C, but neither the pressure nor the brief electric pulse of the printer caused any problem, probably because the conditions are only applied for microseconds.

In practice, the equipment has to drop both binder and drug onto the cellulose powder and 30 to 40 layers are needed for each pill, but several pills can be printed in one powder bed. The equipment could conceivably be scaled up to make many more pills simultaneously. Equally, the ability to make many small batches with precisely varied properties would be useful for pharmaceutical companies performing formulation studies.

The workers have found that the line spacing of the printer head is critical to the release profile of the drugs, which allows even more specific design of pills. Cross-contamination between batches is also eliminated, because the operator would simply slot in a different drug cartridge, much as one can switch between a black or colour cartridge for printer a computer [*Chem Br*, **33**(No.6)(1997)p.18]. ❑

HKK

Renewable source of human neurons created

Dinah W Y Sah of Signal Pharmaceuticals, San Diego and Jasodhara Ray and Fred H Gage of the Salk Institute for Biological Studies, La Jolla, Calif., have "immortalized" human nerve cells, providing a renewable source of human neurons that may expedite testing of drugs for treating neuro-degenarative diseases.

They have engineered a tetracycline-sensitive oncogene into nerve cells from human fetal brain before growing the cells in culture. When growth factors and nutrients were added to the medium, and tetracycline to shut off the oncogene and stop cell proliferation, the cells differentiated along three pathways, one leading only to neurons, another only to glia, the brain's structural cells, and third to both neurons and glia. Manipulation of the culture medium could force differentiation in one direction. According to Sah, the ability "to produce a pure dish of human neurons" is most important for drug discovery. However, being able "to make a cell line that is going to differentiate into two different types of neurons will be of extraordinary use" in studying regeneration of neurons [*Chem Eng News*, **75** (No. 23)(1997) p. 25]. ❑

HKK

New technique maps the body electric

Nathaniel Reichek *et al.* at the Allegheny General Hospital, Pittsburgh, USA have introduced Hall-effect imaging (HEI), strategy for combining ultrasound with magnets and electrodes to map variations in the electrical conductivity of tissues.

The variations may allow clinicians to distinguish tumours, fatty plaques, or areas of ischemia from normal tissue, a process which is difficult with ordinary ultrasound. The technique will also provide better contrast than ultrasound, while retaining a cost advantage over magnetic resonance imaging (MRI). So far, the most complex specimen that has been imaged is a pig kidney, but the technique could eventually have broad applications.

The method makes use of the Hall effect. Electric charges, e.g. ions in biological tissue, follow curved paths when they move in a magnetic field. Because positive and negative charges curve in opposite directions, they diverge, giving rise to a so-called Hall voltage. In biological tissue, an ultrasound beam can create the motion while an external magnet imposes the field. The size of the resulting Hall voltage is determined largely by the tissue's conductivity, the system is actually run in reverse, applying voltage pulses through electrodes and picking up the resulting vibrations with an ultrasound detector. After some mathematical manipulation, the ultrasound signal gives a profile of the conductivity along the direction the detector is pointed. As with conventional ultrasound, the detector must be moved to collect a full 3-*d* image.

Like ultrasound, HEI requires a continuous acoustic path from skin to imaged tissue, so it cannot see through bones or the air in lungs. The technique also requires a magnet and a voltage pulser, which are not needed for conventional ultrasound. But because HEI stimulates acoustic waves in the tissue, the ultrasound needs to travel only one way rather than round trip, as is in conventional ultrasound imaging. It will give HEI deeper penetration and better resolution. The method's best strength is believed to be in its sensitivity to conductivity variations.

When conventional ultrasound imaging of the interior of a blood vessel reveals a bulge then it is difficult to tell whether that bulge is just a harmless fibrous lesion, or whether it is actually a more dangerous fatty plaque. Now, one could potentially use this technique, because there is a big difference in conductivity between these two types of tissue. It is also proposed to use HEI to observe the stages of tumour development, to diagnose ischemic (oxygen-derived) heart tissue, and to distinguish breast tumours from cysts.

The system when tested on a slice of bacon revealed the fat and muscle layers with greater contrast than ultrasound could. It is hoped that HEI will be used to diagnose scar tissue and other abnormalities of the heart [*Science*, **276**(1997) p.681]. ❑

HKK

New study links slimming drugs to heart disease

The study, carried out by the Mayo Clinic in Rochester, Minnesota, found that a combination of the slimming drugs fenfluramine and phentermine, known as 'fen-phen' and prescribed to 18 million people a year, may cause thickening of the heart valves allowing blood to leak back into the heart. The drugs alter the way the body metabolises serotonin, which can cause heart valve damage if it enters the blood stream.

Manufacturers, Smith Kline Beecham, Wyeth-Ayerst, Medeva, Seatrace, Gate, Abana, Richwood, Ion and AH Robins, of these slimming drugs are being sued in the US for failing to warn consumers about dangerous side effects which have been the cause of heart disease in 24 otherwise healthy women. The lawsuit alleges that the companies failed to tell doctors and consumers that the US Food and Drug Administration (FDA) has approved the drugs for separate use only. Combinations have not been tested and do not have FDA approval. The suit also covers a third drug, dexfenfluramine, an alternative to fenfluramine.

The FDA has warned doctors about combination prescribing and called on the manufacturers to change their labelling. The agency has received reports of 33 women with heart valve defects who had been taking fen-phen for as little as one month. There is 'no conclusive evidence of a cause and effect relationship' and therefore, FDA is not demanding withdrawal of drugs from sale. [*Chem Ind*,(**No 14**)(1997),p 542]. ❑

HSDK

High dose of vitamin can cause permanent nerve damage

According to the study, by the committee on Toxicity (COT), taking high doses of vitamin B6 for several months damages peripheral nerves, leading to muscle weakness,tingling, loss of balance and numbness. The symptoms are reversible, but very high doses can cause permanent damage. On the recommendation by COT, Food Advisory Committee (FAC) has fixed the limit of daily intake of vitamin B6 to be 10 mg, which has been accepted by the food safety minister of UK government and is drawing up legislation to control levels of vitamin B6 in dietary supplements.

There are a large number of vitamin B6 supplements freely available in the market, some providing doses of 250 mg. The new law will limit the dose, and supplements will have to carry lables warning about the possible dangers of exceeding the 10 mg limit. People who need extra vitamin B6 because of inherited medical conditions will be able to obtain high-dose pills on prescription. According to lobby group Consumers for Health Choice, women who self-medicate themselves with large amounts of vitamin B6 to combat premenstrual syndrome could lose out. David Bender, a nutritional biochemist at University College London, says that the use of vitamin B6 to combat premenstrual syndrome should be tackled by medical authorities, however, 10 mg is a sensible limit for dietary purposes. [*Chem & Ind*, **No(14)**(19997),p 545]. ❑

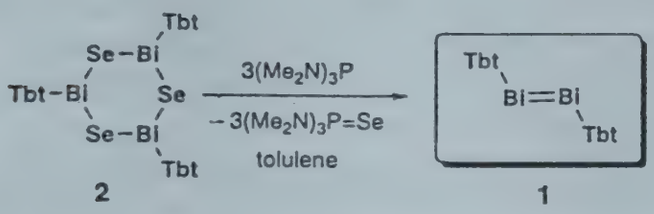
HSDK

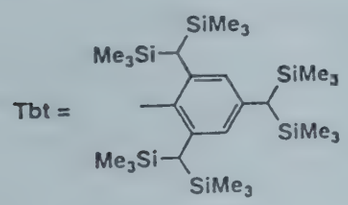
First Bi-Bi double bond obtained

Double bonds between non-metals are often seen for the lighter main-group elements of the periodic table, but for heavier elements, the double bond has not been observed probably because the overlap between the atomic p-orbitals becomes increasingly difficult and destabilizes the formation of the molecular π orbitals. But, bismuth, the heaviest non-radioactive element, has proved to be an exception and has become the first sixth-row main-group element to form a stable bond between two bismuth atoms.

A team of Japanese chemists comprising Norihiro Tokitoh, Yoshimitsu Arai, Renji Okazaki (University of Tokyo, Tokyo 113, Japan) and Shigeru Nagase (Metropolitan University, Tokyo 192- 02, Japan), has succeeded in creating a Bi-Bi double bond by treating a Se_3Bi_3 ring bearing crowded substitutes (**2**) with hexamethylphosphorous triamide in toluene at 100°C. After heating the solution for 12 hours, it turned purple and the dibismuthene (**1**), which precipitated on cooling, was isolated.

According to these researchers, in the dibismuthene, RBi=BiR, the reactive Bi=Bi moiety is surrounded by bulky 'R' groups, where R is 2,4,6-tri(bis(trimethylsilyl)methyl)phenyl (denoted as





'Tbt' in the structure **2**) which suppresses its oligomerization.

Dibismuthene is quite stable in the solid state, retaining its purple colour for several hours on exposure to the open air, but it undergoes slow reaction with atmospheric oxygen to form a Bi_2O_2 ring.

The report has shown the possibility of double bond formation by other heavy main-group elements also. The Tokyo team isnow planning to obtain the first stable antimony-antimony double bond [*Science*, **277** (No. 5322) (1997) 78-80; *Chem Eng News*, **75** (No.27) (1997) 27]. ❑

BSA

A clean method for aromatic brominations reported

A team of researchers in England has reported that supported zinc bromide is an effective and eco-friendly catalyst for the production of bromo-aromatic intermediates used in the manufacture of pharmaceuticals, agrochemicals, and other speciality chemical products. This joint group of chemists from the University of York and Contract Chemicals, Merseyside (UK), has discovered that zinc bromide supported on mesoporous silica or acid-activated montmorillonite clay is a fast, efficient and selective catalyst for room-temperature bromination of aromatic substrates. Not only this, the catalyst is reusable also [*Chem Commun*, (1997) 1203].

According to these researchers, the catalyst also improves the para- to ortho-isomer ratio, as observed by them in the bromination of bromobenzene. According to Professsor James H. Clark of Yales University, 'by giving higher selectivity, the catalyst makes a better utilization of bromine and minimizes the amount of unwanted ortho isomer that is wasted'. The catalyst is effective in hexane also.

The research director of the Merseyside firm, Tony W. Bastock, being more concerned about the economics of the bromination reaction, considers the reuse of the supported zince bromide as a significant advantage, specially for industrial applications [*Chem Eng News*, **75** (No. 28) (1997) 36]. ❑

BSA

Report on the growth of petrochemical products demand by 2001 AD

A study by Federation of Indian Chambers of Commerce and Industry (FICCI) on "Growth Potentials in the Indian Petrochemical Industry" undertaken by Haldia Petrochemicals Limited, describes that the demand for petrochemical products in India would go from 5.1 million mts in 1995 to 9 million mts by the year 2001 AD. It also mentions that the demand for petrochemical would emanate mostly from agriculture, infrastructure, and consumer sectors.

In the agriculture sector, the use of extensive sprinkler system, drip irrigation, linear systems for ponds and canals, geo textiles and sacking, crating for agricultural produce would increase the demand for petrochemical products. The secondary sector, i.e. the food processing industry has the capability for enhancing the demand for plastics exponentially.

In the infrastructure sector, the power and cable sector would trigger off a boom for wire and cable compounds. The boom in the telecommunication sector would increase the demand for telephone cable.

The building industry also require petrochemicals such as, pre- fabricated components, pre-fitted toilets, etc. FICCI has identified favourable factors for the growth of petrochemical industry in India. These include feedstock availability, natural gas, ethane/propane, natural gas liquids, naphtha, and refinery gases.

The feedstock position in India is complicated because of multifarious use of the same feedstock. India is short of petroleum feedstock and, therefore, it is the largest component of the country's import. The use of feedstock as raw materials for petrochemical industry has become centre of attraction as the value addition is maximum in this case [*Chem Week*, **42** (No 46) (1997) p 90]. ❑

HSDK

National Dairy Research Institute (NDRI), Karnal: Annual Report 1996-1997

National Dairy Research Institute (NDRI) is the premier organization that provides R&D support for Dairy Development programmes of the Nation. It has gained prominence as the front ranking research organization world over. The Institute works in close liaison with various National and International developmental agencies. It catalyses close interaction among scientists, students, farmers and dairy industry for orchestrating dairy development process in a harmonious manner. The Institute aims to providing R&D support towards generation and dissemination of knowledge towards improved national milch herd for milk production enhancement, greater productivity of dairy industry and management aspects of the dairy profession leading to the social, economic, and environmental benefits to the Nation as well as contributing towards manpower of development programme. The Institute was established keeping in view the following objectives:

(i) To undertake basic and applied research in the area of Dairying, covering Production, Processing, Economics, and Management.

(ii) To develop Dairy Farming systems for different agro-climatic conditions and demonstrate models for transfer of technology.

(iii) To organise and conduct programmes at under-graduate and post-graduate levels in various branches of dairy sciences.

(iv) To organise short -term specialised training programmes and vocational courses.

(v) To collaborate with National and International agencies for dairy Research and Development (R&D).

(vi) To provide consultancy to Dairy Industry, Dairy Farmers and other Dairy Development Agencies. and

(vii) To act as a referral centre on Dairy Research.

Salient Achievements of NDRI during 1996-97

In Infrastructure the Achievements are:

(i) A new Auditorium having seating capacity of 950, two conference rooms, two meeting rooms with projection facilities is constructed.

(ii) The Artificial Breeding Complex with rearing facility of 140 bulls, collection and processing of high quality semen and maintaining a semen bank became fully functional.

(iii) The erection of equipments and commissioning of Model Dairy Plant with the capacity of 60,000 lits milk / day has been completed.

(iv) A state-of-the art Livestock Genoma Laboratory, well equipped to carry out molecular biology research, has been established under the NARP project at DCB Division of the Institute.

(v) An "Environmental Research Laboratory" with special facilities for *in vivo* estimation and monitoring of methane production from animals has been set up at DCN Division of NDRI.

(vi) A new horticulture unit has been set up to provide on the job training to farmers in the field of horticulture.

(vii) The Agricultural Research Information System Cell, created under the AEGIS of ICAR to enable scientists and students to have a quick access and free exchange of information was made functional.

In R&D the Achievements Are as Follows:

(i) Milk production in lactating cattle and buffaloes could be increased to the extent of 30 per cent by administration of recombinantly derived bovine somatotrophin, without any adverse effect on the composition of milk and reproductive health of the animals.

(ii) GT specific DNA probe has successfully revealed DNA fingerprints in cattles and buffaloes.

(iii) Heat exchanger for preconditioning of milk, coagulant supply unit, and integrated ventury mixer for continuous cheese making has been developed for better recovery and quality of cheese.

(iv) A kit has been designed for the detection of various adulterants like urea, sugar, glucose, starch, neutralizers, hydrogen peroxide, carbonate, bicarbonate, animal body fat and vegetable oils under field conditions.

(v) A simple and rapid PCR based method for detection of coliforms and *Mycobacterium* basis has been developed.

(vi) An instant Banana Milk Shake Powder developed at Southern Regional Station, Bangalore, as an effective treatment for intolerance against certain carbohydrates is marketed by Kerala Milk Federation under brand name *Milma*.

In the Field of Education the Achievements are:

(i) A two and half year National Dairy Diploma course has been started at the SRS, Bangalore.

(ii) Seventeen B Tech (DT), 34 M Sc (Dairying) and 22 Ph D (Dairying) students obtained degrees from NDRI.

(iii) Under the auspices of Centre of Advanced Studies, the Dairy Technology and Dairy Cattle Breeding Divisions organised several short-term courses for improving the competence of teachers from SAUs.

(iv) Training opportunities were provided to visiting scholars from various countries. In-plant training facilities were also imparted to the students from sister institutions and SAUs.

(v) Several new scholarships were instituted for the students of NDRI.

The Other Miscellaneous Achievements Are as follows:

(i) All India Dairy Husbandry officers' workshop was organised during 15-16 November 1996 in the area of Animal Husbandry, Dairy Processing, and Management.

(ii) Under the Farming System Research Project, 6297 milk producing households were covered for transfer of new scientific know-how on milk and crop production.

(iii) The twentieth Dairy Mela was held during 14-15 March 1997 under the theme "Dairying for Rural Development". More than 12,000 farmers and farm women participated.

(iv) During the period, 2149 trainees were trained by Krishi Vigyan Kendra of the NDRI on different aspects of Animal Husbandry and Dairying, Agriculture, Horticulture, Bee-keeping, Fisheries and Home Science.

(v) 'Farmers Day' and 'Women in Agriculture Day' were organized by KVK for the benefit of farmers and rural women.

(vi) A major Pilot Project on Technology Assessment and Refinement through Institution-Village Linkage Programme (IVLP) was initiated in five villages around Karnal to identity available resources, production systems, problems in agriculture and animal husbandry, and gender related issues affecting rural development. ❑

HSDK

Report of the Working Groups of Information Society Forum of the European Commission

The European Commission decided to set up the Information Society Forum in February 1995 in order to create a new and authoritative source of reflection, debate and advice on the challenges of the Information Society.

The Forum consists of 128 members drawn from five main fields of activity:

- Users of the new technologies: industry (banks' retail, maritime etc), public services, consumer groups, small and medium-sized enterprises and the professions
- Social groups: academics, employers organisations and trade unions, youth groups, regional and city representatives
- Content and service providers: publishers and authors, film and TV producers, broadcasters, computer software producers and information service providers
- Network operators: fixed telecommunications, cable TV, mobile and satellite operators
- Institutions: members of Parliament, of the Economic and Social Committee of the Committee of the Regions and the data protection Commissioner.

Six working groups have been formed whose members have given their views under the following heads:

- the impact on the economy and employment;
- basic social and democratic values in the "virtual community,"
- the influence on public services
- education, training and learning in the Information Society
- the cultural dimension and the future of the media

sustainable development, technology and infrastructure

The European Commission has published the first Annual Report and the supplementary report (working group's reports) which can be obtained from the Information Society Forum Secretariat (European Commission, Information Society Activity Centre, 200 Rue de la Loi, BU 24, 2/70, B-1049 Brussels. The full texts are also available on the ISPO web server at: URL: http:/vww. ispo. cec be/info-forurm/pub.html

Summary of the last installment of the report of Working Group VI under the head "Sustainable development, technology and infrastructure" is given in this issue.

Summary of Report of the Working Group VI: Sustainable development, technology and infrastructure

Introduction

In preparing the Forum's first annual report, the working groups have largely concentrated on the issues of sustainability and on technology and infrastructure. The aim has been to analyse the two issues in terms of the interaction between sustainable development and the use of Information and Communications Technologies (ICT)

In particular, three major items were addressed by three rapporteurs: sustainability issues by Professor Radermacher, "From Hard to Soft" by Professor Chryssolouris and infrastructural developments by Mr R Bomer and Professor Chryssolouris. The report reflects the contributions of these rapporteurs and the Group's discussions on a draft report prepared by the Chairman, Mr Carrelli.

The main points of discussion

As is widely known, the concept of sustainable development derives from a growing awareness that "current generations should meet their needs without compromising the ability of future generations to meet their own needs" (that is, without causing resource depletion, environment destruction and extreme energy consumption).

The Maastricht Treaty has endorsed the principle of a harmonious and balanced development of economic activities, sustainable and non-inflationary growth while respecting the environment.

The concept of sustainable development is linked to the development of an Information society in an important way. Only information and communication technologies offer major opportunities for reducing material use and for a less "resource-intensive" lifestyle.

Societies face a choice between achieving sustainability or managing chaos, and a shift to the right sort of Information Society can be a major contribution to achieving sustainability. While it may also involve a shift in the balance of trade in favour of developing countries, Europe can not hide behind protectionist barriers. The shift to sustainability must be worldwide, with Europe playing a leading role.

The "dematerialisation" flowing from the new technologies and related new forms of social and economic organisation may reduce the impact of the so-called "rebound effect" (erosion through increased consumption of saving made possible by technology innovation). Technological innovation offers the means to produce more value, more efficiently with less material resources. On the other hand, social innovation must also take place. Careful study is required because there are risks as well as benefits.

The shift from a hard, manufacturing and material-intensive economy to a soft, information-rich service economy will inevitably disrupt traditional industries. The goal must be to help all actors (workforce, industry and educational institutions) actively to contribute to shaping new models.

A key element will be the development of "information infrastructure" defined in the broadest sense as "a system of equipment for transport and diffusion of information for any type of application, including hardware, software, computers and programmes for network and service management".

The new information infrastructure will not be a single new network, superseding everything already existing. It will be a network of interconnected networks. It must ensure digital end-to-end connection and widespread access.

The basic components of the information infrastructure derive from a least three types of networks: telecommunications networks (traditional as well as alternative), terrestrial and satellite television broadcasting networks and the Internet. The existing net-

works will evolve, coexist, interconnect with each other and make the best use of available technology.

The lack of take-off services for the Information society is not due to lack of infrastructure, but rather to lack of applications and slowness in developing a mature information culture.

The responsibilities of network operators, service providers and content providers will have to be clearly defined. The Group has proposed a model for reference.

Technical aspects examined in the report cover the role of standards and aspects related to symmerty-asymmetry of bandwidth.

From the economic point of view, market demand is considered as the main driver for investment (at least in the long term), but it is recognized that the market will not guarantee access everywhere and a balanced trade-off between market pull and a policy-driven approach is recommended.

Since it is not commercially viable to deploy optical fibres everywhere, a middle ground approach should be explored based on the development of "telecentres" in each local community.

The concept of universal access and universal service obligation is analysed as an evolving phenomenon, because of both technological evolution and social dialogue.

The role of the regulatory framework must be investigated so as to promote investments in the new technologies and to help the development of new services at lower costs.

No doubt the possibilities offered by technical progress and ICT will help to fulfill the obligations of sustainable development. but infrastructure development is not sufficient in itself and there is a need to explore the economic and social implications of the Information Society, and not only its technological effects.

This need lay behind the creation of the Forum and the Commission should give it extra attenuation. Further studies should be promoted from the economic and social perspective as well as from the technological point of view. [Annual Report of the Information Society Forum Secretariat, European Commission, Information Society Activity Centre, 200 Rue de la Loi, BU 24, 2/70, B-1049 Brussels].

Announcement

Ninth Annual General Meeting of Materials Research Society of India

The Ninth Annual General Meeting (AGM) of the Materials Research Society of India (MRSI) will be held at the Indian Institute of Technology Madras, Chennai, during 11-13 February, 1998, organised by the Madras Chapter of MRSI. The AGM will include a plenary address, invited talks and poster sessions. During the AGM, a Theme Seminar will be held on the theme 'Advanced Materials' with special emphasis on Building Materials Electronic Materials, Magnetic Materials, Polymers and Composites. Many invited lectures will be delivered by MRSI medal winners during AGM, covering the subject areas: Bio-materials, Building Materials, Ceramic and Glasses, Composites, Electronic Materials, Magnetic Materials, Metals, Polymers, Processing Technologies, Thin Films, Materials Characterisation and Fracture.

Further details and the registration form may be obtained from:

Dr V V Varadaraju
Chairman, MRSI - Madras Chapter
Materials Science Research Centre (MSRC)
IIT Madras, Chennai - 600 036

Two satellite symposia will be held on February 10, 1998 on "Alternate energy Materials " at IGCAR, Kalpakkam and "New Materials and Processing Technologies" at IIT Madras, Chennai.

The satellite symposium on "Alternate Energy Materials" will focus attention on: Hydrogen Storage Materials, Energy options- vis-a-vis material resources, Solar photovoltaics, Fuel Cells, Thermoelectric sources, Processing - Properties - Performance of materials and Advanced energy management systems.

Further details may be obtained from:

Dr Baldev Raj
Director
Metallurgy and Materials Group
Indira Gandhi Centre for Atomic Research
Kalpakkam - 603 102, India
Tel.: (04114) 40234
Fax: (04114) 40301/40356/40360

Dr S Ramaprabhu
Magnetism and Magnetic Materials Laboratory
Department of Physics
Indian Institute of Technology Madras
Chennai 600 036, India
Tel: (044) 2351236 Extn. 3240
Fax: (044) 2350509/2352545

The satellite symposium on "New Materials and Processing Technologies" will cover" New Materials: Microporous and mesoporous solids, Nano materials, Rapidly solidified materials, Bio-materials and Advanced Engineering Ceramics Processing Technologies: Superplasticity and Dynamic Farming, Directional solidification, Surface Engineering, Self Propagating High Temperature Synthesis and Intelligent Processing of Materials.

Further details may be obtained from:

Prof K A Padmanabham/Prof O Prakhabar
Conveners
Metallurgical Engineering Department
Indian Institute of Technology Madras,
Chennai 600 036, India
Fax: 044 - 2350509/2352545 ❑

BOOKS

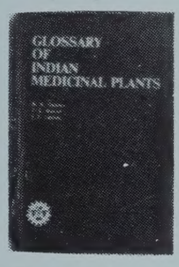
on

PHARMACEUTICAL & MEDICAL SCIENCES

from

NISCOM

		Price (Rs.)	Postage (Rs.)
* The Treatise on Indian Medicinal Plants			
	Vol.-I	250.00	10.00
	Vol.-Ii	300.00	10.00
	Vol.-III	350.00	15.00
	Vol.-IV	400.00	15.00
* Compendium of Indian Medicinal Plants			
	Vol.-I	300.00	15.00
	Vol.-II	550.00	15.00
	Vol.-III	600.00	15.00
	Vol.-IV	750.00	15.00
* Glossary of Indian Medicinal Plants		180.00	10.00
* Supplement to Glossary of Indian MedicinalPlants		80.00	10.00
* Second Suplement to Glossary of Indian Medicinal Plants		160.00	12.00
* Status Report on Cultivation of Medicinal Plants in NAM Countries		300.00	15.00
* Status Report on Aromatic and Essential Oil-bearing Plants in NAM Countries		400.00	15.00
* Medicinal Plants: Bibliography of CSIR Countributions (1950-1987)		60.00	10.00
* Heal with Herbs		50.00	3.00
* The useful Plants of India		300.00	15.00
* A Dictionary of the Flowering Plants in India		63.00	10.00
* Drug Addiction with special reference to India		50.00	10.00
* Tropical Diseases		600.00	20.00
* Medicinal & Aromatic Plants Abstracts (International Journal) Annual Subscription		500.00	-
* The Wealth of India (Raw Materials) (XI Vols. with 3 supplements)		4070.00	-



Order should be accompanied by Demand Draft/Money Order/IPO made payable to **National Institute of Science Communication, New Delhi** and sent to:

Sales & Distribution Officer
National Institute of Science Communication, CSIR
Dr K.S. Krishnan Marg, New Delhi 110012
Phones:5785359, 5786301/7 Ext 287,288
Gram:PUBLIFORM , Telex:031-77271, Fax:011-5787062

Printed & Published by Director, NISCOM, on behalf of National Institute of Science Communication and Printed at the printing unit of NISCOM, New Delhi - 110012

KEEP ABREAST OF THE LATEST DEVELOPMENTS IN BASIC AND APPLIED SCIENTIFIC RESEARCH

READ NISCOM JOURNALS

Monthly Journals	Annual Subscription Rs	US$
◆ Journal of Scientific & Industrial Research	500	200
◆ Indian Journal of Chemistry,Section A	600	240
◆ Indian Journal of Chemistry, Section B	600	240
◆ Indian Journal of Experimental Biology	600	240
◆ Indian Journal of Pure & Applied Physics	500	200
Bimonthly Journals		
◆ Indian Journal of ChemicalTechnology	300	120
◆ Indian Journal of Engineering & Material Sciences	300	120
◆ Indian Journal of Biochemistry & Biophysics	300	120
◆ Indian Journal of Radio & Space Physics	300	120
◆ Medicinal & Aromatic Plants Abstracts	500	200
◆ Journal of Intellectual Property Rights	1000	400
Quarterly Journals		
◆ Indian Journal of Marine Sciences	250	90
◆ Indian Journal of Fibre &Textile Research	250	90

For Subscription contact:

Sales & Distribution Officer
National Institute of Science Communication
Dr K S Krishnan Marg, New Delhi 110012
Phones: 5785359, 5786301-7 Ext. 287, 288
GRAM: PUBLIFORM:Telex 031-77271
Fax:011-5787062

DL-18020/97
RNI-4596/57